

FINAL REPORT

**TRANSFER OF DECANTING TECHNOLOGY RESEARCH TO OIL
SPILL RESPONSE ORGANIZATIONS AND REGULATORS**

by

SL Ross Environmental Research Ltd.
Ottawa, ON

for

Minerals Management Service
Technology Assessment and Research Division
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SUMMARY

In U.S. Territorial waters mechanical recovery (using containment booms and skimmers) is the preferred method used to clean up oil spills. Skimmers operating in waves often recover a large amount of water, both in the form of emulsions and free water. Recovered water dramatically reduces the temporary storage capacity available for oily fluids offshore. This report describes the final study of a multi-year program to research decanting of water from recovered oil spill fluids offshore.

Between 1997 and 2004 a series of lab-scale and mid-scale experiments with and without the use of emulsion breakers were completed that gave some quantitative insight into the oil/water separation processes occurring in temporary storage devices. The objective of these experiments was to determine the optimum time to decant the water and maximize the available on-site storage space during a skimming operation as well as the efficacy of adding emulsion breakers into the recovery stream to allow separation and decanting of emulsified water. The results¹ indicated that:

- “Primary break” (the initial separation of the recovered fluid into a layer containing most of the oil and a layer containing most of the free water) occurs within a few minutes to one hour, depending of the physical characteristics of the oil.
- Rapidly decanting this free water layer, in appropriate situations, may offer immediate increases of 200 to 300% in available temporary storage space.
- Initial Total Petroleum Hydrocarbon (TPH) concentrations in the decanted water depended on the physical properties of the oil; they ranged from 100 to 450 mg/L for the most viscous oil to 1400 to 3000 mg/L for the least viscous. These declined by a factor of approximately 3 after one hour of settling, and by a factor of approximately 5 after one day.
- The use of a demulsifier injected into a recovery system, combined with decanting, substantially reduced the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.
- The application of demulsifier did not appear to affect the time required to achieve “primary break”.
- The efficacy of the demulsifier was a strong function of free water content. In these tests, if the free water content exceeded about 55%, the effect of the surfactant was substantially reduced.
- The degree of emulsion breaking achieved increased with increasing mixing energy applied to the recovered fluids. Increasing the flow rate (and hence turbulence level), adding mechanical mixing energy and increasing the length of the flow path all resulted in increased emulsion breaking.

¹ The efficiency of emulsion breaking chemicals in resolving water-in-oil emulsions is highly parent oil/surfactant specific and can be strongly affected by the dosage of the demulsifier and the weathering processes that an emulsified oil has undergone. The tests conducted for this study investigated the effects of mixing energy and other physical parameters on the efficacy of three emulsion breakers with one water-in-oil emulsion specifically “engineered” for the project and one emulsion formed from a crude oil. The conclusions drawn are only strictly valid for these combinations of demulsifier and emulsion.

- The results indicated that the use of a demulsifier approximately doubled TPH concentrations in the decanted water.
- The formation of micelles by the demulsifier surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure the concentration of the demulsifiers in the decanted water make definitive conclusions about the partitioning of the demulsifier between oily and water phases impossible. The following general conclusions could be made:
 1. A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
 2. The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as in the 1000's of ppm.

The discharge of oil by vessels into the sea is prohibited under MARPOL 73/78, with the following exceptions:

- The oil content of the discharge does not exceed 15 ppm (except in Special Areas, such as the Antarctic or the Great Lakes, where no oil content is permitted);
- "...the discharge into the sea of substances containing oil, approved by the Administration, when being used for the purpose of combating specific pollution incidents in order to minimize the damage from pollution. Any such discharge shall be subject to the approval of any Government in whose jurisdiction it is contemplated the discharge will occur."

The United States Federal On Scene Coordinator (FOSC) is granted an exclusion from the National Pollutant Discharge Elimination System (NPDES) permit requirement for discharges under 40 CFR 122.3(d) which covers, "Any discharge in compliance with instructions of an On-Scene Coordinator pursuant to 40 CFR 300 (The National Oil and Hazardous Substances Pollution Contingency Plan) or 33 CFR 153.10(e) (Pollution by Oil and Hazardous Materials)"

Most Area Contingency Plans have detailed instructions on the USCG policy regarding decanting and many contain sample forms for requesting permission to decant from various State and other authorities. The exception seems to be the Great Lakes, in which decanting does not appear to be encouraged.

During skimming/decanting operations, an operational unit moves, collecting oil and discharging decanted water generating an effluent plume. The effluent, which contains concentrations of toxicants, is discharged inside the containment boom below the sea surface as the vessel proceeds at a given speed for the duration of the skimming operation. The jet of decanted water exiting the discharge hose mixes immediately with the surrounding water and the resulting plume spreads horizontally and vertically in the water column by turbulent diffusion.

Though toxicant concentrations in the effluent may exceed toxic levels initially, these concentrations decline quickly with time through dilution, falling below toxic levels and ultimately declining to background levels. Scenarios and computer modeling were used to estimate both the effective plume width and effective plume depth at the point at which

contaminant concentrations in the plume dilute to the thresholds for acute lethality for each toxicant (1 ppm for Total Petroleum Hydrocarbons [TPH] and 60 ppm for demulsifier).

The results of the plume dilution analyses suggest that the impact of operating a single skimming unit for the first three days of the response operation would be a toxic footprint in the upper water column, ranging in size from 0.04 km² to 0.8 km². The lower end of this range is associated with discharges containing 50 to 100 ppm TPH with the depth at which these plumes dilute below toxic concentrations predicted to be generally less than 10 m. The higher end of the range is associated with discharges containing 1,000 to 2,000 ppm TPH, with depths at which the plume dilutes below toxic concentrations predicted to be in the 20 to 30 m range. The impact derives largely from the oil contained in the decanted water: the modeling results suggest that risks from the demulsifier would be much less than from the oil, due largely to the demulsifier's lower toxicity. As expected the predicted size of the impacted area depends on the rate at which oil is collected and the decanted water is discharged, but the area of impact can vary by a factor of 2 to 3 depending on the concentration of hydrocarbons in the decanted water.

The implication of this research for oil spill response is that it may be possible to greatly reduce downtime for offshore skimming operations caused when the available temporary storage systems are filled with fluids containing large amounts of water. The legislated requirements for onsite temporary storage systems could also ultimately be reduced by the use of these results, resulting in considerable savings in operating and disposal costs for Oil Spill Response Organizations (OSROs). Knowing that the separated water can be decanted quickly will optimize onsite recovery operations and greatly reduce the volume of fluids requiring disposal. In fact, the removal of most of the free and emulsified water from the recovered product would greatly enhance the likelihood that it could be recycled, as opposed to requiring disposal.

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DISCLAIMER

This report has been reviewed by the U.S. Minerals Management Service staff for technical adequacy according to contractual specifications. The opinions, conclusions, and recommendations contained in this report are those of the authors and do not necessarily reflect the views and policies of the U.S. Minerals Management Service. The mention of a trade name or any commercial product in this report does not constitute an endorsement or recommendation for use by the U.S. Minerals Management Service. Finally, this report does not contain any commercially sensitive, classified or proprietary data release restrictions and may be freely copied and widely distributed.

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1. INTRODUCTION

The preferred approach to cleaning up an oil spill is to contain and thicken the oil slick(s) with booms and then place skimmers in the oil or emulsion to recover it. The recovered fluids are placed in temporary storage containers for transfer to larger storage vessels or for direct input into the waste recycling and disposal system. Offshore skimmers often recover a large amount of water, both in the form of water contained in emulsified oil and free water. In some cases, the transfer pump built into the skimming system can impart enough energy to cause additional emulsification of the recovered fluids. The problem is that the recovered water (both emulsified and free) dramatically reduces the temporary storage space available at the site of skimming operations. This can result in having to stop skimming prematurely when the storage capacity is reached and having to wait until empty temporary storage containers arrive at the response site. The treatment and separation of recovered water onsite is the largest area of neglected technology in mechanical response today (Schulze et al. 1995).

In the relatively low-energy environment within a temporary storage device, the recovered fluids will begin to separate into layers of oil, emulsion and water. Periodically discharging the separated water back into the containment boom can considerably extend the available storage space and increase the effective use of available resources to remove oil from the water surface. The discharge of this decanted water is regulated in the United States and Canada.

There is an optimum time at which the separated water should be discharged, or decanted, from the temporary storage device. This optimum time maximizes the amount of water that can be removed from the container, minimizes the oil content of the discharged water, and minimizes the time that the storage is "out of service". The decision when to decant may also depend on whether or not sensitive resources could be affected by the dispersed oil or dissolved demulsifier concentrations in the discharged water.

This report presents the results of a study that completes a program of research on decanting recovered oil spill fluids spanning over seven years. The focus of this report is the regulatory aspects of decanting during offshore spill response operations in US waters. Guidance is provided for On Scene Commanders in making the decision whether or not to allow the discharge of decanted water.

Section 2 presents a detailed summary of the experimental studies of decanting and emulsion breaking. Section 3 summarizes the regulatory regime governing decanting of recovered oil spill fluids offshore in the United States and Canada. Section 4 presents a series of hypothetical scenarios in which decanting could be used to improve the efficiency of an offshore mechanical response operation and presents model results for the dilution of the water discharged overboard. Section 5 estimates the potential environmental impacts from the discharged water.

2. DECANTING RESEARCH SUMMARY

This section consists of a review of the past experimental research on decanting of water from recovered oil spill fluids.

2.1 Test Series Summary

The first test series (involving lab-scale tests in flasks in 1997 and large-scale tests at Ohmsett in 1998) investigated the decanting of mixtures of recovered oil and water and gave some quantitative insight into the oil/water separation processes occurring in simple temporary storage devices (SL Ross 1998 and 1999). The objective of these tests was to determine the optimum time to decant the free water and maximize the available on-site storage space during a skimming operation.

That many skimmer operations are, sooner or later, faced with recovering a water-in-oil emulsion was addressed in the second test series. These emulsions can easily contain 70 to 80% water that is tightly held and may not separate out, even after standing for days or months. This emulsion will quickly fill the available temporary storage space, even after decanting the free water layer, with a product that contains mostly water. The available temporary storage space could be further extended by using chemical emulsion breakers (also called demulsifiers) to cause the water-in-oil emulsion to break into oil and water phases, followed by decanting of the water separated from the emulsion.

Although some skimmer systems (notably the Framo Transrec 350) incorporate demulsifier delivery systems, the dynamics of the separation process are not well understood. Literature reviews of the demulsification of oil spill emulsions are presented by Payne and Phillips (1985) and SL Ross et al. (1992a). Preliminary research into the process performed in the early-1990s (SL Ross 1991 and 1992b), Strom-Kristiansen et al. 1993, Lewis et al. 1995a and 1995b) gives some guidance on the concentrations of demulsifier required for rapid breaking and the importance of mixing energy to the process; however, these preliminary studies were not pursued further. Readers interested in further details of past work on demulsifiers are encouraged to read the literature review in SL Ross 2002.

The second series of experiments, in both the lab using a scale-model piping network simulating an offshore recovery and transfer system, and again at Ohmsett, was designed to assess the effectiveness of an oil spill emulsion breaker on water-in-oil emulsions and the injection/mixing/settling regimes required for optimum water-removal performance. The ability of emulsion breaker addition to reduce pumping heads and the effects of demulsifier addition on the oil content of decanted water were also assessed. Various injection locations (skimmer head, discharge hose, tank inlet, etc.) and mixing technologies (static in-line, impeller, etc.) were investigated.

The third set of tests was designed to study the partitioning of the active ingredient in demulsifiers between the oil and water phases in recovered fluids. Four different demulsifiers were tested on different emulsions using both the bench-scale piping model

and large-scale tests at Ohmsett. These tests were designed to measure the concentration of demulsifier in decanted water as a function of several operational variables.

The results and conclusions from each of the three experimental test series are now described in greater detail.

2.2 1998 Decanting Tests at Ohmsett

Following an extensive series of bench-scale tests in glass flasks in 1997 (SL Ross 1998), a series of tests was conducted at Ohmsett in November 1998 to investigate the decanting of oil/water mixtures recovered by weir skimmers (SL Ross 1999).

2.2.1 Methods

The following parameters were varied during the tests:

1. Two circular weir skimmers:
 - Desmi Terminator - nominal Oil Recovery Rate (ORR) in waves of 20 m³/hr (90 US gpm)
 - Pharos GT-185 - nominal ORR in waves of 10 m³/hr (45 US gpm)
2. Two slick thicknesses:
 - 20 mm and 100 mm (representing the thickness expected in a single vessel sweep system and a large, multi-vessel offshore boom system respectively)
3. Three oil types:
 - Hydrocal, Calsol and Sundex (with viscosities of 1100, 13,000 and 300,000 mm²/s [cSt] respectively at the test temperature)
4. Two wave conditions:
 - Wave #1 (15 cm x 11.3 m with a period of 2.8 s) and Wave #2 (15 cm x 4.6 m with a period of 1.7 s)

A 15-m (50-ft.) section of 24-in. conventional containment boom was deployed in a square at the north end of the Ohmsett basin, between the main and auxiliary bridges (Figure 1). Two recovery devices were deployed in the boomed area: a GT-185 skimmer and a Desmi Terminator skimmer (Figure 2). Only one skimmer was operated for a given test.

The skimmer discharge was directed to the eight oil recovery tank cells located on the auxiliary bridge (Figure 3). The separated water from the oil recovery tanks was either dumped back into the Ohmsett test basin, or directed to a temporary holding tank for water sampling. The time when the filling of each tank cell was started and finished was recorded. The depth of fluid in each cell was measured and recorded. Simultaneously with the filling operation, two minutes after tank cell #7 was filled, the separated water was decanted until the discharge from the bottom visibly contained oil. The remaining



Figure 1: Boomed test area between main and auxiliary bridges.

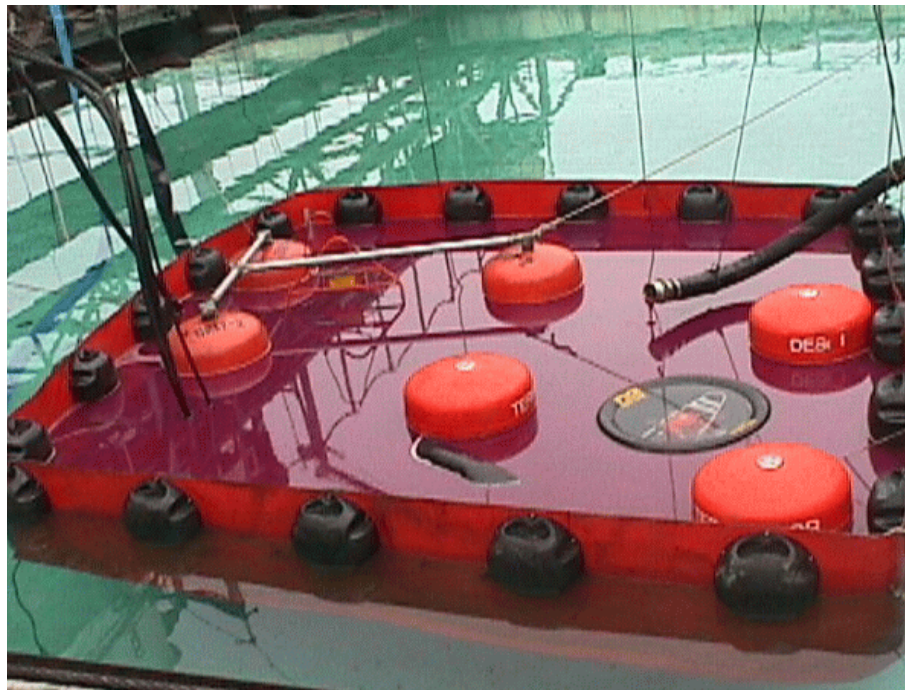


Figure 2: Skimmers in boomed test area with Calsol oil. Desmi Terminator at front right, Pharos GT-185 at back left.



Figure 3: Recovery tank on auxiliary bridge.



Figure 4: Mixing tank for decanted water sampling.

oil recovery tank cells were decanted in sequence at 5, 10, 15, 30, 45, and 60 minutes after the time they each reached full.

For selected cells in each test, the decanted water was directed to a temporary holding tank on the deck beside the auxiliary bridge (Figure 4). When all water from a selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with a bladed impeller and allowed to settle for five minutes to allow large droplets of oil, from the end of the decanting process, to surface. The surface oil was removed with a sorbent pad and then the temporary holding tank was drained. A small water sample, for oil content analysis, was taken when half the water had been drained. The purpose of this was to estimate the average concentration of "permanently dispersed" oil in the decanted water - i.e., the droplets that would not rise out and re-coalesce with the slick if the decanted water was discharged back into a boomed area. During three of these tests (one for each of the three test oils) duplicate samples of the decanted water were placed in vertical columns for 24 hours and then drained. The water from the bottom, middle and top of the columns was sampled and was analysed for oil content.

The depth of oily fluid remaining in each cell was measured (these depths, combined with the initial depths, were used to calculate the volumes of recovered product, decanted water and oil remaining). The idea was to determine the time required for "primary break" of the skimmer discharge product. "Primary break" is the point at which the bulk of the lower density phase has risen to the top and most of the higher density phase has settled to the bottom; both phases typically contain small droplets of the other phase at this point. At primary break, the interface between the two phases may not yet be distinct. Each oil recovery tank cell was mixed and sampled to determine the water content of the fluid remaining. The various samples collected were analysed using standard Ohmsett procedures for water content of oil (ASTM D1796), oil concentration in water (EPA 413.1), density (ASTM D1298), interfacial tension and surface tension (ASTM D971), and kinematic viscosity (ASTM D2983).

2.2.2 Summary of Results

Complete details of the test results may be found in the project report (SL Ross 1999) which may be obtained using the MMS web site www.mms.gov/tarprojects/.

Figure 5 shows typical water separation results for one of the test oils used (20 mm thick Calsol slicks). The four graphs show the results obtained with the GT-185 skimmer in wave No. 2 (Test 2) and wave No. 1 (Test 3), and with the Desmi skimmer in wave No. 2 (Test 4) and wave No. 1 (Test 5). Each plot shows the following, plotted against elapsed time from when the tank cell was filled to when it was decanted:

- Percent Decanted - $[\text{volume of water decanted} / \text{volume of fluid recovered}] \times 100\%$;
- Decanted Water Volume; and,
- Water Volume Remaining - $[\text{volume of fluid recovered} - \text{volume of water decanted}] \times \text{water content of remaining fluid}$.

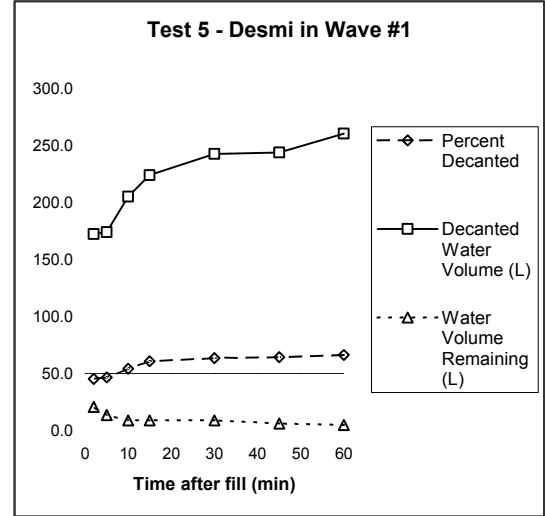
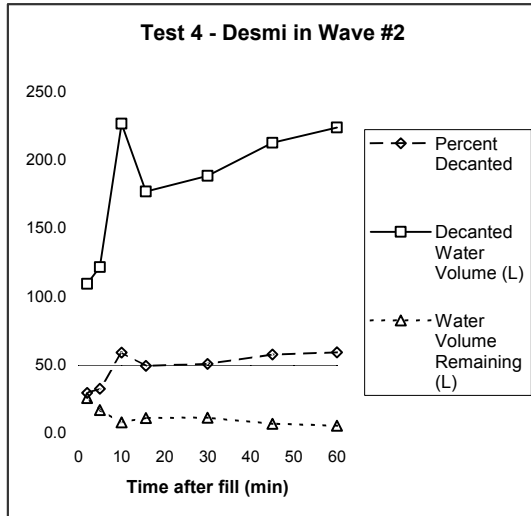
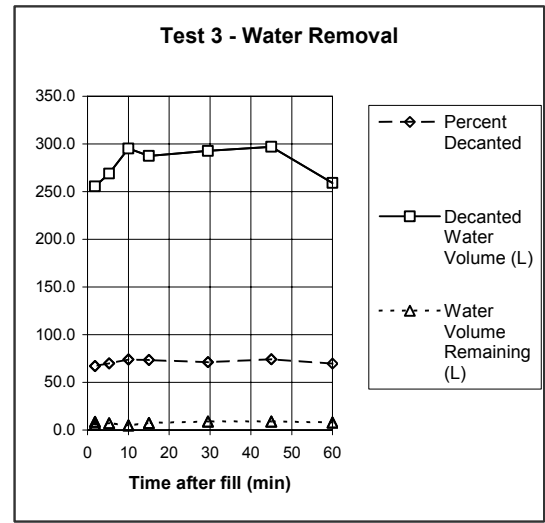
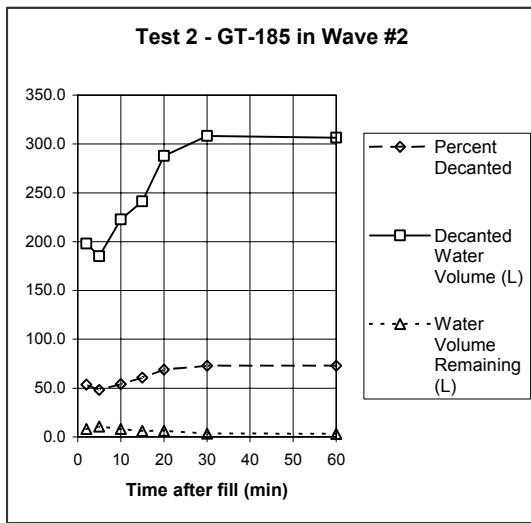


Figure 5: Water Removal from Fluid Skimmed from 20 mm Calsol Slicks (note that the units of the y-axis depend on the curve, as noted in the legend)

All the plots clearly show that most of the water can be decanted from the recovered fluid with a delay of only 30 minutes or so. Skimmer type and wave period did not seem to greatly affect the decanting. For the thin slicks of the less-viscous oils the separation of the water from the recovered fluid was essentially complete in 15 to 30 minutes. Up to 60 minutes was required for primary break with the thicker, more-viscous slicks.

For the thinner slicks, the trend appeared to be faster separation with increasing oil viscosity. This was probably because the recovered product consisted of oil droplets entrained in a continuous water phase. The more viscous the oil the larger the oil droplets in the water; larger oil droplets rise faster than smaller ones.

For the thicker slicks, the situation appeared to be different. With these slicks, the skimmers recovered much less water, and it is likely that the recovered fluid stream consisted of water droplets suspended in a continuous oil phase. In this case oil viscosity controlled the settling rate: higher oil viscosities meant longer settling times. With the highest viscosity oil, the water was semi-permanently emulsified in the oil and did not settle appreciably over the 60-minute test.

Doubling the volume of fluid placed in the tank cell [equivalent to doubling the height of the fluid in the tank cell] had no discernible effect on decanting times or the final percent water decanted. Agitating the receiving tank with wave action also had no discernible effect on water separation rate or amount.

Figure 6 illustrates typical oil-in-water concentration data obtained from analysing the decanted water samples. The highest concentrations of oil in the decanted water occurred when skimming Calsol slicks. Initial concentrations were in the 1400 to 3000 mg/L range. These declined to 400 to 1000 mg/L after one hour of settling. The lowest concentrations of oil in the decanted water were for the Sundex oil. In these tests, the concentrations were initially in the 100 to 450 mg/L range, declining to about 50 to 150 mg/L after 60 minutes of settling. When skimming Hydrocal the concentrations of oil in the decanted water were initially about 1000 mg/L. These declined to approximately 200 mg/L after one hour. Allowing 24 hours settling further reduced oil concentrations in the decanted water to 30 to 70 mg/L for Calsol, 2 to 20 mg/L for Sundex and 30 to 100 mg/L for the Hydrocal test series. Doubling the volume of fluid recovered in each cell did not appreciably affect the oil-in-water concentrations.

2.3 2001 Decanting Tests with Emulsion Breakers

In July 2001, a second series of experiments was carried out to investigate the use of emulsion breakers injected into an oil spill recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett). The experiments were designed to assess the injection/mixing/settling regimes required for optimum water-removal performance from a meso-stable water-in-oil emulsion (see Fingas et al. 1998 for the characteristics of the various emulsion states) treated with an oil spill demulsifier. Various injection locations (skimmer head, discharge hose, tank inlet, etc.) and mixing technologies (static in-line, mechanical, etc.) were investigated.

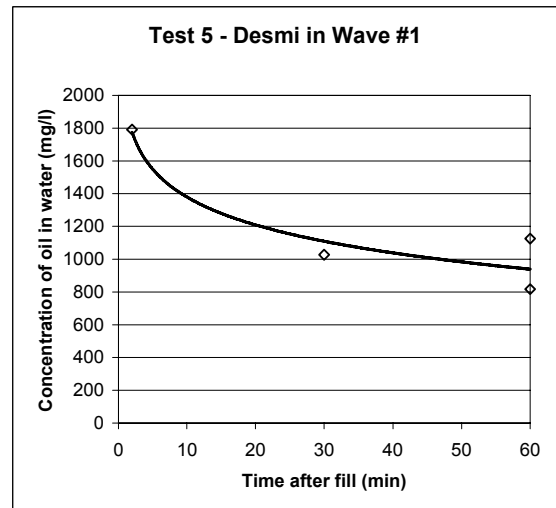
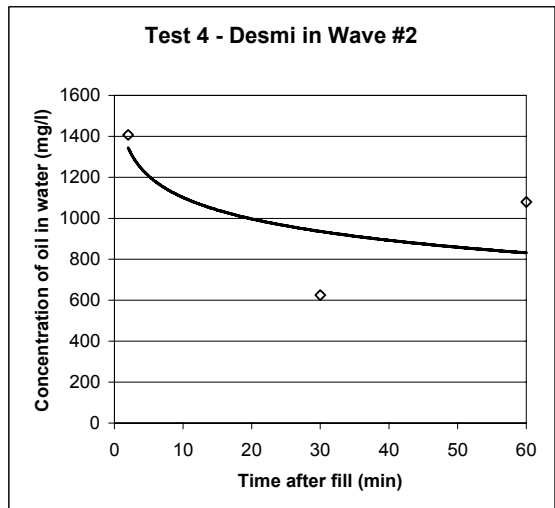
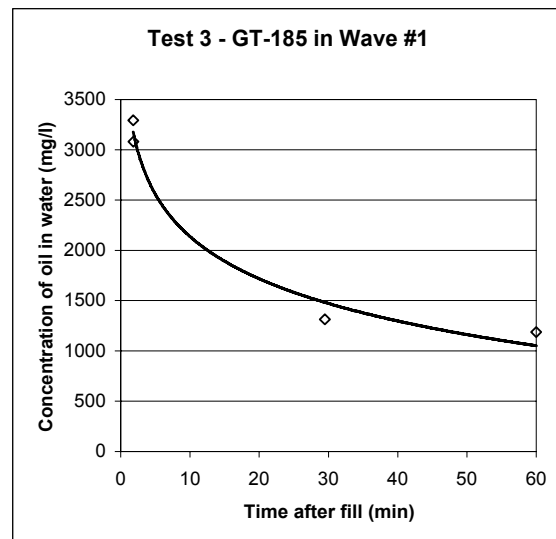
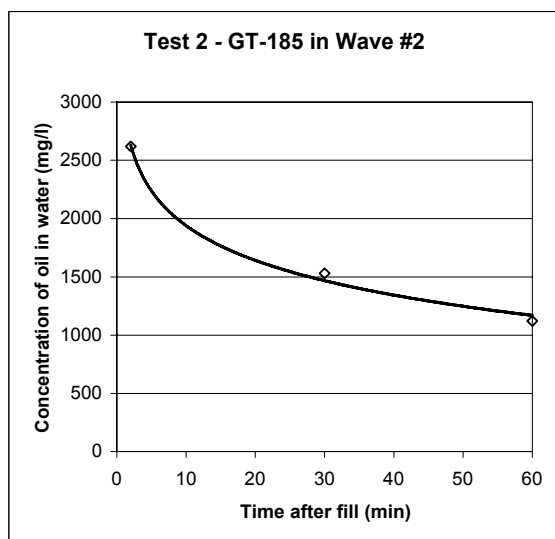


Figure 6: Oil Content of Decanted Water from 20 mm Calsol Slick

The scaled laboratory tests involved pumping water-in-oil emulsion and free water through a scale-model piping loop consisting of ½-inch copper and plastic tubing of various lengths, an in-line mixer and eight settling tanks (Figures 7 and 8). Three different types of pumps (gear, double-diaphragm and progressing cavity) were used. Demulsifier was injected at various locations, and the fluid was decanted and measured to determine the efficiency of emulsion breaking achieved. These tests are not discussed in this report. They may be found in SL Ross 2002 that can be obtained using the MMS web site www.mms.gov/tarprojects/.

At Ohmsett, a Desmi Terminator skimmer was used to recover the same emulsion as used in the laboratory tests, from the water surface, using different slick thicknesses, two wave heights and different recovery rates (to vary the turbulence in the recovery system). A static in-line mixer was used for some tests, and in others a bladed impeller was used to add extra mixing energy to the recovered fluids. Demulsifier was injected into the recovered fluid at various locations. The recovered fluid was allowed to separate in the recovery tanks and measured to determine the demulsifier efficiency.

2.3.1 Ohmsett Experimental Methods

At the beginning of the Ohmsett tests, and subsequently as required, large batches of emulsion were prepared. A gear pump was used to prepare the emulsion, since large quantities of a consistent quality were required on a daily basis. The procedures are detailed in the report (SL Ross 2002). Based on a series of emulsion formation and stability tests and experience gained from the laboratory tests 2.5% Bunker C was added to the Hydrocal oil in order to create a suitable parent oil for the preparation of a meso-stable water-in-oil emulsion. The function of the Bunker C was to provide asphaltenes to stabilize the small water droplets in suspension in the oil. A sample of the first batch of emulsion prepared was allowed to sit for 24 hours, and showed no signs of breaking. The target properties of the emulsion were: 50% (vol.) water content with a viscosity of approximately 1000 cP at a shear rate of 1 s⁻¹ at 21°C. A 50% water content was chosen because it could be prepared reasonably quickly using the gear pump technique with little risk of inverting the emulsion, as can occur with higher water contents.

The same test setup and procedures used in the 1998 tests were employed for the 2001 tests, with some additions to accommodate the emulsion breaker. Pressure transducers were also installed, located at either end of a 13-m (42.5-foot) section of the skimmer discharge hose to measure pressure drop. For some tests, the skimmer discharge was directed through a Lightning Series 45 Model 4 Type 12H in-line mixer. The separated water from the oil recovery tanks was directed to a temporary holding tank for water sampling, and then sent to a holding tank for eventual treatment and disposal to the sanitary sewer. This was to avoid adding dissolved emulsion breaker to the 10,000 m³ of Ohmsett tank water, which may have negatively affected subsequent test programs.

Demulsifier (Alcopol O 70% PG, aka Drimax 1235B a solution of sodium diisooctyl sulfosuccinate in propylene glycol/water) was injected using a fixed-rate (1 L/min = 0.25

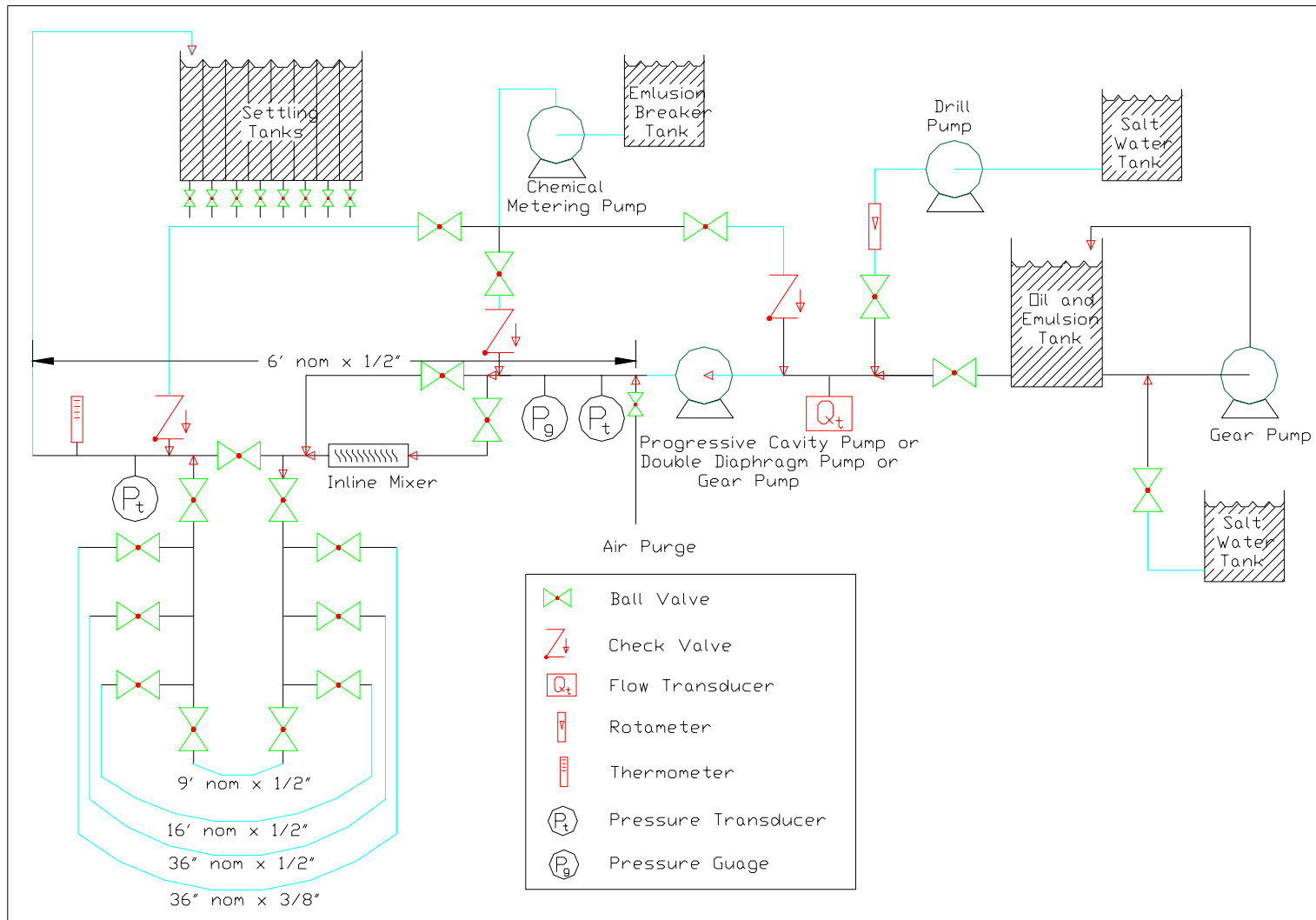


Figure 7: Schematic of Laboratory Scale-model Piping Network Setup



Figure 8: Photo of laboratory scale-model piping network.



Figure 9: In-line mixer on deck connected to discharge hose just before recovery tanks.

US gpm) peristaltic pump into the recovered fluid in one of two locations: directly into the skimmer weir or into the discharge hose just before the wye upstream of the inline mixer (Figure 9). As with the 1998 tests, for some runs the decanted water was sent to a sampling tank, where it was mixed thoroughly, and sampled for oil content analysis. As well, this tank and mixer was used to thoroughly mix the entire contents of some recovery tank cells, to assess the effects of additional mixing energy on emulsion breaking.

2.3.2 Summary of Results

The efficiency of emulsion breaking chemicals in resolving water-in-oil emulsions is highly parent oil/surfactant specific and can be strongly affected by the dosage of the demulsifier and the weathering processes that an emulsified oil has undergone. The tests conducted for this part of the study investigated the effects of mixing energy and other physical parameters on the efficacy of one emulsion breaker with one water-in-oil emulsion specifically “engineered” for the project. The conclusions drawn below are only strictly valid for this combination of demulsifier and emulsion. The tests showed that use of a demulsifier injected into a recovery system, combined with decanting, can substantially reduce the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling. Table 1 is a summary of the results from these Ohmsett tests.

The efficacy of the demulsifier was a strong function of free water content, beyond an upper and a lower limit. In these tests, if the free water content exceeded about 60%, the effect of the surfactant was substantially reduced. If no free water was present, the level of turbulence generated by the flow was insufficient to promote emulsion breaking. Free water contents of greater than about 33% was required to reduce the bulk viscosity of the fluid to the point where the flow regime was turbulent, and mixing energy was supplied to promote emulsion breaking. It is possible that this phenomenon is demulsifier-specific and would not be observed with a different demulsifier. It is also possible that this phenomenon is related to the solvent used in the demulsifier, and use of a different solvent would yield different results.

The degree of emulsion breaking achieved increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking. The use of in-line mixers further increased the removal of emulsion water. The application of mechanical mixing energy, using a bladed impeller, after placing the recovered fluid in a tank, also increased demulsification.

The best location for injection of the demulsifier was at the skimmer pump for recovered fluids containing up to 50% free water to maximize the amount and time of the mixing applied. For recovered fluids containing more than 60% free water, decanting the free water followed by the application of mechanical energy worked best. Primary break occurred in only a few minutes (2 to 5 in the lab tests, less than 15 for the Ohmsett tests). The application of demulsifier did not appear to affect this.

Table 1: Summary of Ohmsett demulsifier test results

Test No.	Demulsifier Injection Point	Demulsifier Dosage (Fluid: Demulsifier)	Wave Type	Inline Mixer	Initial Slick Thickness (mm)	Final Slick Thickness (mm)	Fluid Recovery Rate (gpm)	Estimated Free Water (%)	Recovered Emulsion Water Content (avg %)	Extra Mix Water Content		Oil content of Decanted Water			Back Pressure (psig)	Pressure Drop (psi/ft)
										Tank 4 Lab/vol	Tank 1 Lab/vol	2 min.	30 min.	60 min.		
1	No	None	1	No	19	104	140	48	51	-	-	214	72	337	6.4	0.011
2	No	None	2	No	21	26	106	60	57	-	-	490	220	327	7.1	0.020
3	Skimmer	992	1	No	62	90	144	68	52	-	-	543	574	343	7.1	0.025
4	Skimmer	732	2	No	90	70	152	66	57	-	-	1086	514	404	7.1	0.020
5	Discharge	732	1	No	70	57	139	69	70	-	-	1079	629	479	7.0	0.019
6	Discharge	676	2	No	64	27	137	64	71	-	-	1376	606	543	7.0	0.022
7	Before mixer	990	1	Yes	27	18	144	72	71	-	-	1113	433	432	10.2	0.031
8	Before mixer	826	2	Yes	18	8	142	69	66	-	-	871	560	176	9.9	0.022
9 (dupl. 8)	No	787	2	Yes	20	5	135	66	67	-	-	1052	304	305	9.6	0.020
10	No	None	1	No	105	62	157	47	52	-	-	-	294	181	8.7	0.034
11	No	None	2	No	89	25	147	45	61	-	-	-	1110	301	8.1	0.028
12	Skimmer	1669	1	No	88	14	287	37	44	-	-	-	357	233	18.5	0.134
12A	Skimmer	624	1	No	100	28	135	8	54	-	-	-	-	-	10.4	0.050
13	Skimmer	646	2	No	53	18	134	44	55	-	-	2543	655	618	6.9	0.015
37	Skimmer	650	2	Yes	47	0	134	58	46	-	-	882	136	104	9.3	0.015
38 (dupl..37)	Skimmer	605	2	Yes	15	36	125	54	43	-	-	763	530	570	8.8	0.016
39	Skimmer	670	1	Yes	36	39	139	56	45	39/36	38/37	-	-	-	na	na
40	Skimmer	2397	1	Yes	87	130	323	54	33	36/23	42/32	-	-	-	37.6	0.142
41	Skimmer	2750	2	Yes	130	109	371	47	35	45/27	34/27	-	-	-	37.4	0.133
42	No	None	2	Yes	159	115	377	39	39	45/48	48/42	-	-	-	38.5	0.150
43	Skimmer	582	2	Yes	171	85	78	43	52	36/31	33/??	-	-	-	3.6	-0.035
44	Discharge	2854	2	No	86	73	385	75	43	57/27	39/42	-	-	-	20.8	0.159
45	Discharge	2800	1	No	172	68	377	32	50	45/41	40/37	-	-	-	23.2	0.192

The Ohmsett experiment results indicated that the use of a demulsifier increased oil-in-water concentrations by approximately a factor of two in the decanted water (Figure 10). Although it is not known what portion of each oil-in-water reading was associated with dissolved demulsifier in the water, the decanted water did contain a significant amount, as evidenced by its tendency to foam when agitated.

As long as the recovered fluid contained at least 33% free water, the pressure drops due to skin friction in the tubing and hoses approximated those expected for flowing water. The use of an in-line mixer significantly increased backpressures.

2.4 2003 Tests to Study the Partitioning of the Demulsifier

Demulsifiers are surface-active, or surfactant, chemicals that can be added to ‘break’ or ‘resolve’ the emulsion back into separate oil and water phases. Demulsifiers function by destabilizing or disrupting the film of precipitated asphaltenes and/or resins that are known to stabilize water-in-oil emulsions. For a demulsifier to function effectively, it must be able to come into intimate contact with the oil-water interface around the water droplets in emulsified oil. The surfactant chemicals within a demulsifier therefore need to be introduced into the emulsified oil and thoroughly mixed with it.

Being surfactants, the active ingredients of demulsifiers are not truly soluble in either water or oil; the minimum surface free energy is achieved when the surfactant molecules are orientated at an oil/water interface. This property results in their surface-active nature. The molecules of surfactants can orientate into “micelles” or “reverse micelles” to accommodate their solution in either water or oil. These are less preferred arrangements than orientation at an interface, but this is critical to the behaviour of these chemicals. It is therefore possible for surfactants to be present in bulk in either the water or oil phases, as well as at the oil/water interface. This tendency is known as ‘partitioning’. Of course, if a demulsifier is effective, it greatly reduces the amount of oil/water interface originally in a water-in-oil emulsion, and much of the surfactant would move back into the bulk liquid phases. The proportion of surfactant that will be present in the oil or water phases depends on the relative proportion of oil and water phases that are available for them to be dissolved in as well as the surface active properties of the demulsifier itself.

The use of surfactants in demulsifiers for breaking recovered emulsified oils is therefore quite complex. The surfactants in demulsifiers are normally in the form of a concentrated solution blended in a solvent. The solvent in the blend allows the surfactants to transfer into the emulsified oil. In the inevitable presence of free water during oil recovery operations some surfactant may move directly into the free water and will not perform its intended function of breaking the emulsion. This tendency can be minimised if the proportion of free water is kept to a minimum. The transfer of surfactants into the emulsified oil can be difficult because of the highly viscous nature of many emulsified oils. Once inside the bulk of the emulsified oil, the surfactants need to be able to contact the oil/water interface at the surface of the entrained water droplets. Some surfactant may orientate to form reverse micelles within the oil – this is effectively ‘lost’ from the

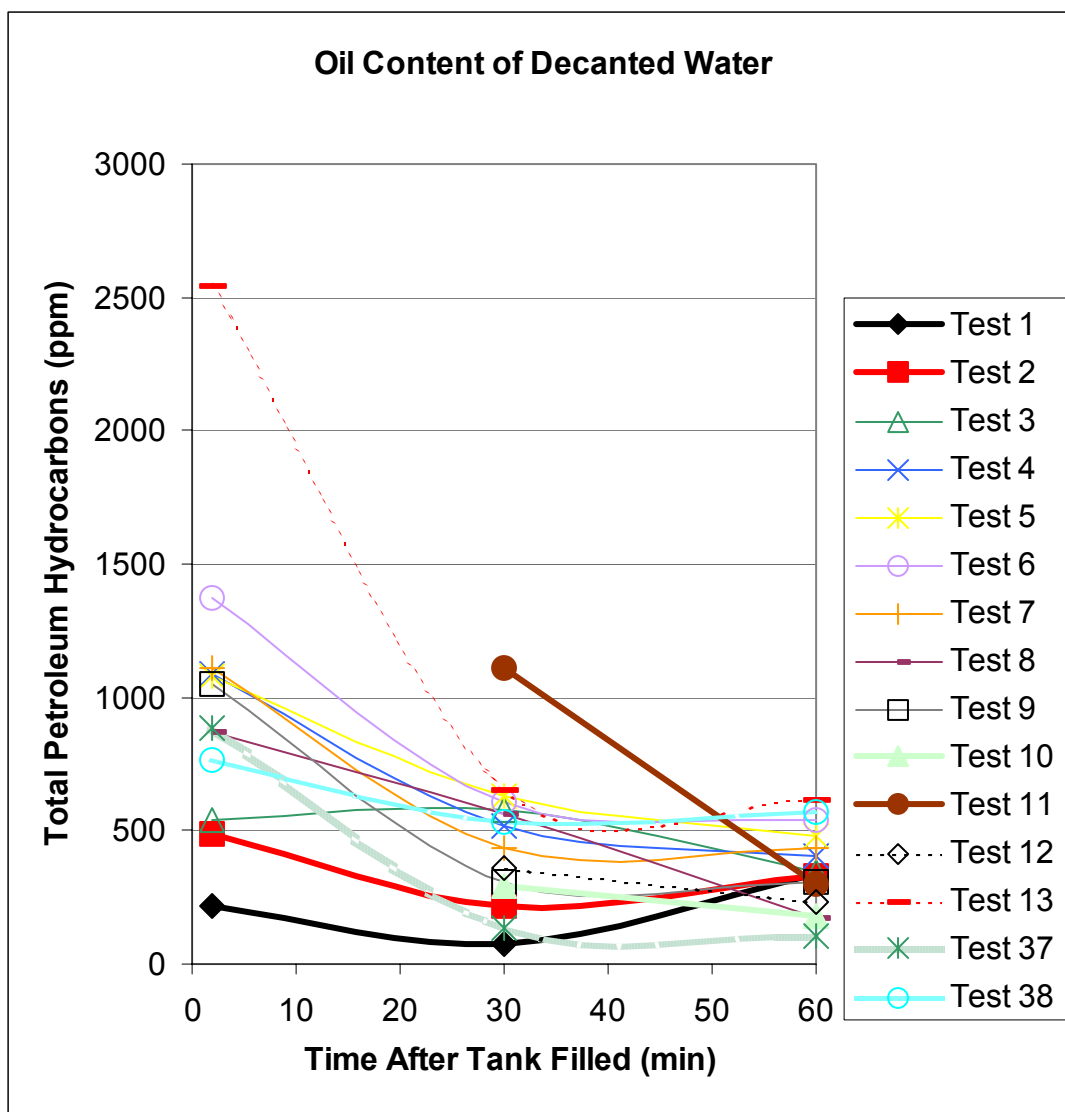


Figure 10. TPH Concentrations in Decanted Water from Emulsions Treated with Demulsifier (Baseline tests, i.e., no demulsifier, are #'s 1,2, 10 and 11)

emulsion-breaking process unless mechanical agitation introduces it to the oil/water interface.

The surfactants within demulsifiers can therefore partition into any of the phases that they may encounter during spilled oil recovery:

- Into the free water
- Into the oil phase
- Into the emulsified water phase that is subsequently separated by gravity

If the bulk of the surfactants in the demulsifier remain with the oil, there should be no problem with their use; the recovered oil will be collected and disposed of. However, if the majority of the surfactants partition into the separated water (either initially free or entrained water), they will be discharged into the environment if the separated water is decanted overboard. Some partitioning is an inevitable consequence of surfactant behaviour. The relative tendency to partition, either as individual molecules or as micelles and reverse micelles between oil and water is very dependent on molecular structure.

Some demulsifiers, such as sodium diisooctyl sulfosuccinate, are strong ionic surfactants that have a relatively high toxicity to some marine organisms. If a recovered fluid consists of 50% free water and 50% of an emulsion containing 75% water and all the emulsion breaker used to treat it (typically dosed at 1:400 demulsifier:emulsion) transfers into the water, the decanted water could contain some 1400 ppm of demulsifier. Discharge regulations in some jurisdictions would not permit the decanting of such water to the ocean in normal circumstances. Other demulsifiers, such as the EO/PO (ethylene oxide/propylene oxide) copolymers are non-ionic, and tend to be much less toxic.

Some emulsions are easier to break with ionic surfactants, and some are easier to break with non-ionic surfactants. The environmental consequences of demulsifier use will depend on:

- Their effectiveness in breaking emulsions
- Their partitioning behaviour into the different water and oil phases
- Their toxicity to marine organisms
- The potential for dilution of the decanted water in the receiving water body

The purpose of the final series of tests reported here was to study the partitioning of different emulsion breakers injected into a recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett).

2.4.1 Analytical Test for Demulsifier in Water

Prior to carrying out the study, it was necessary to develop a simple, inexpensive test to measure the concentration of demulsifier in decanted water. The approach taken was to adapt a technique developed to measure the concentration of dispersants in Ohmsett tank water (SL Ross 2003). This method involved measuring the interfacial tension between a highly refined mineral oil (USP, or pharmaceutical grade) and the water containing the surfactant using a DuNouy ring apparatus (ASTM –D971). The interfacial tension value

obtained is compared to a plot of interfacial tension vs. concentration of prepared aqueous solutions of the demulsifier in question to obtain an estimate of the concentration of the demulsifier.

Figure 11 shows the calibration curves prepared for the four demulsifiers considered for use in the lab-scale tests. Although the interfacial measurement technique gives a reasonable fit of the data for most of the demulsifiers to a power law relationship of the form:

$$\text{Concentration} = C_1(\text{IFT})^{-C_2} \quad (1)$$

Where: C_1 and C_2 are demulsifier-specific constants

it is clear that the relationships will not give very accurate results at concentrations of demulsifier above about 100 ppm. This is because there is very little change in interfacial tension with a large change in demulsifier concentration above this point, most likely due to the fact that the demulsifier has exceeded its Critical Micelle Concentration (CMC) and the oil/water interface is saturated with surfactant molecules. A difference of only 0.3 dynes/cm in interfacial tension in the 1.5-dyne/cm range results in a 300+ ppm difference in calculated demulsifier concentration.

Despite its shortcomings, the interfacial tension technique was used as the method for estimating the concentrations of demulsifier in the decanted water for this study. This was primarily because the other available techniques (High Pressure Liquid Chromatography [HPLC], complex titrations, etc.) are very expensive and time consuming.

2.4.2 Parent Oil Blend for Emulsions and Demulsifiers Used

In the previous series of tests using demulsifiers it was observed that the demulsifiers could not completely resolve the emulsions created using a blend of 95% Hydrocal and 5% No.6 fuel oil (used to add asphaltenes). This was presumed to be because this parent oil contained no aromatic compounds (Hydrocal is a de-aromatized lube stock) to act as a sink for the asphaltenes displaced from the water/oil interface by the demulsifier. As such, a series of emulsion stability tests with various mixtures of Hydrocal, No. 6 Fuel Oil (2.5 or 5 % by volume) and automotive diesel (5, 10 or 15% by volume) were conducted to select a mixture that would form a stable, 50 % salt-water emulsion that could be completely resolved by the demulsifiers to be used. Based on the stability results and the demulsifier effectiveness tests, the parent oil blend was selected to be 80% Hydrocal, 5% No. 6 Fuel Oil (aka Bunker C) and 15 % automotive diesel. For some tests, emulsion created using fresh Endicott crude (which met the stability criteria), from Alaska, was also used. The three demulsifiers selected for testing in the lab-scale tests

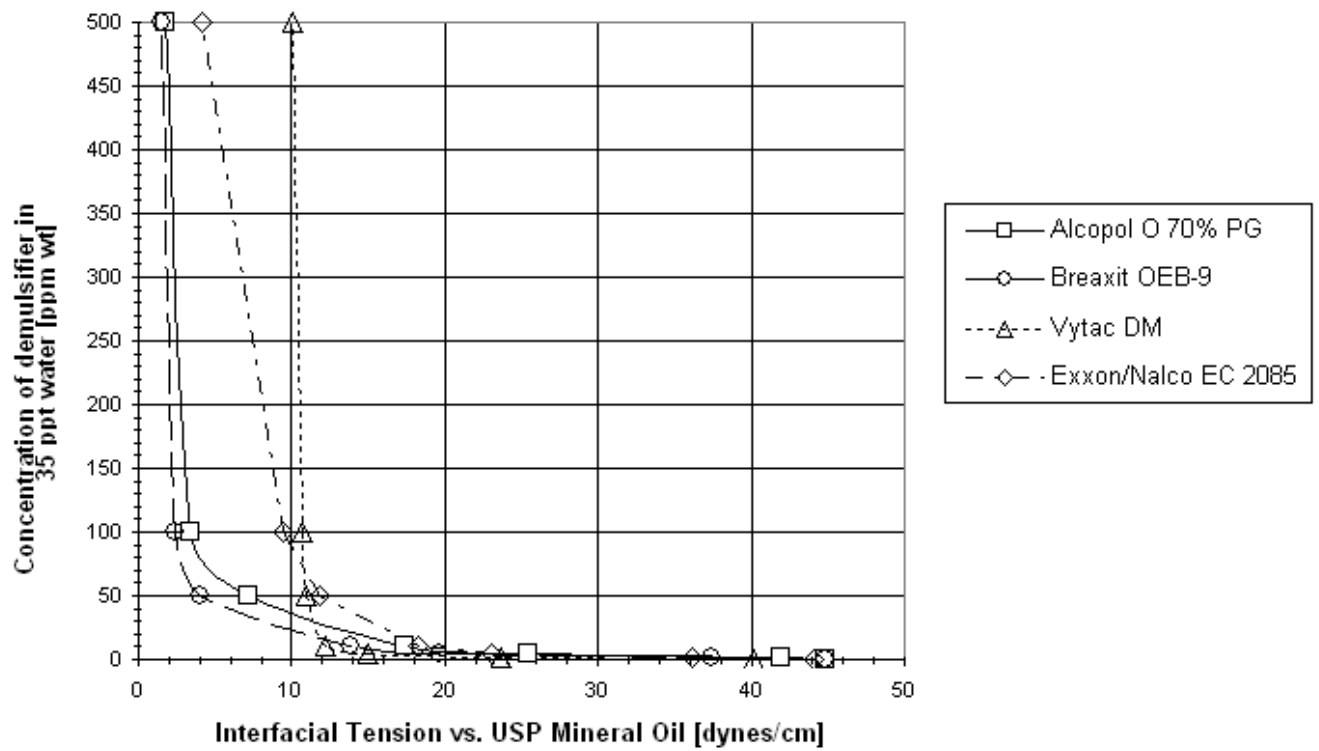


Figure 11: Calibration curve of interfacial tension vs. demulsifier concentration.



Figure 12: Photo of boom triangle and Desmi Terminator skimmer in water.

were: Alcopol O 70% PG (aka Drimax), Breaxit OEB-9 and Exxon Nalco EC2085, an older product specifically blended as a generic production emulsion breaker for Alaska North Slope crudes.

2.4.3 Laboratory Test Results

The apparatus and the procedures used in the laboratory tests are described in detail in the report (SL Ross 2004). To summarize, samples of stable 50% water emulsion prepared using a small gear pump from the parent oils described above were pumped with nominally 50% free water, at measured, pre-determined rates, to the suction of a small progressing cavity pump, representing the pump type used in most weir skimmers. The fluid was then directed through a ½” diameter scale-model piping network consisting of a static in-line mixer, copper pipe and valves, either a 6-foot or 36-foot length of ½” ID plastic tubing and then to six cylindrical receiving tanks where samples were taken at different intervals to characterize the separation of the aqueous phase and the dehydration of the emulsion (see Figures 7 and 8 above). Demulsifier was injected, at different dosages, into the system before the progressing cavity pump using a chemical metering pump.

At pre-determined intervals over one hour, the cylinders were decanted and the volume of water removed was measured. A sample of the water was obtained for determination of the concentration of demulsifier, as described above, and a sample of the oily phase remaining in the cylinder was taken to determine its water content.

A total of 25 test runs were completed using the laboratory scale model piping setup. The complete results may be found in the final report (SL Ross 2004). The following summarizes the findings.

Primary Break

In almost all of the tests, primary break occurred in two to five minutes.

Partitioning of the Demulsifiers

The formation of micelles by the surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure the concentration of the demulsifiers in the decanted water make definitive conclusions impossible. The following general observations can be made:

- A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
- The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as 1000's of ppm.

Effectiveness of the Three Demulsifiers in Breaking Emulsions of the Two Oils

Overall, it was apparent that the Alcopol demulsifier was the best of the three demulsifiers tested on 50% salt water emulsions made from both parent oils (the Hydrocal blend and the fresh Endicott crude). The next most effective demulsifier on the Hydrocal blend emulsions was Breaxit. The Alcopol was better than the Exxon Nalco demulsifier on the fresh Endicott emulsions, and seemed to work as well with the

Endicott as it did with the Hydrocal blend. The effect of the Exxon Nalco product seemed to be to create a very fine dispersion of oil droplets in the water, which made subsequent separation of the oil and water very slow.

Effect of Demulsifier Dose Rate

It was observed that a higher Alcopol dose rate (ca. 2600 ppm) provided better resolution of the emulsion than did a lower rate (ca. 900 ppm). The same was true for the Breaxit demulsifier. In one case with the Exxon Nalco product, the lower dose rate resulted in better breaking of the Endicott crude emulsion than the higher dose did.

Effect of Free Water

As was the case with the previous series of tests, when the free water content in the treated fluid exceeded 55%, the efficiency of the demulsifier was reduced. When the demulsifier was injected into a fluid stream that contained only emulsion, the separation initially was much poorer than in tests where the free water was less than 50%, but after 60 minutes, the demulsifier effectiveness was about the same for both cases.

Effect of Tubing Length

Pumping the treated fluid down either a 6-foot or 36-foot long length of ½”-tubing was the only variation in mixing level used in the lab-scale test series. As was observed in the earlier demulsifier lab-scale tests (SL Ross 2002), better resolution of the emulsion was obtained when the treated fluid was pumped through the 36-foot length than the 6-foot length. This was likely related to greater mixing of the demulsifier and the emulsion in the longer length of tubing.

2.4.4 Ohmsett Test Results

The apparatus and the procedures used in the Ohmsett tests are described in detail in the report (SL Ross 2004) and generally followed those used in the previous tests described above. Only a summary of the equipment and procedures is given here. All tests were conducted in a stationary position (i.e., no towing down the tank).

The test area consisted of 11.5 m (37.5 feet) of 24-inch Globe boom deployed in a triangle (12.5' per side) between the Auxiliary Bridge and the Main Bridge (Figure 12). The boomed area was approximately 6.2 m² (67 ft²). A Desmi Terminator skimmer was placed in the test area and operated from the deck. The skimmer discharge was directed to four of the oil recovery tanks on the Auxiliary Bridge via 3-inch flexible hose. For all tests, the skimmer discharge was directed through a Lightnin Series 45 Model 4 Type 12H in-line mixer. The separated water from the oil recovery tanks was directed to a temporary holding tank for water sampling, and then sent to a holding tank for eventual treatment and return to the tank.

Demulsifiers (Alcopol O 70% PG, aka Drimax 1235B, and Unichem RNB-60425, an emulsion breaker specifically designed for Endicott crude) were injected using a fixed-rate (0.25 gpm) peristaltic pump directly into the skimmer weir. Two different wave conditions were generated during this test series.

At the beginning of the tests, and subsequently as required, batches of emulsion were prepared. A gear pump was used to prepare the emulsion, since large quantities of a consistent quality were required on a daily basis. A blend of 80% Hydrocal 300/5% IFO 380/15% automotive diesel was used as the parent oil for most of the tests. Fresh Endicott crude was used as the parent oil for two tests. A sample of the first batch of Hydrocal blend emulsion prepared was allowed to sit for 24 hours, and showed no signs of breaking.

For a typical test, a pre-determined volume of emulsion was added to the test triangle, the waves were started, then the skimmer was started and make-up emulsion added to the triangle at a rate approximating the skimmer removal rate. Demulsifier was then added to the weir of the skimmer. The recovered fluids from the skimmer were directed to fill different cells in the Recovery Tank sequentially. The time required to fill each cell and its volume was recorded. At selected times after each cell had been filled, they were decanted, and measured to determine the volume of oily phase remaining. A sample of the oily phase was then taken to determine its water content. The decanted water was directed to a temporary holding tank on the deck beside the Auxiliary Bridge. When all water from a selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with a bladed impeller and allowed to settle for five minutes to permit large droplets of oil, from the end of the decanting process, to surface. The surface oil was removed with a sorbent pad and then the temporary holding tank was drained. Two small water samples, one for oil content analysis and one for IFT analysis to determine its demulsifier content, were taken when half the water had been drained from the temporary holding tank.

The complete results for the Ohmsett tests can be found in the final report (SL Ross 2004) and are summarized in Table 2. The ability of emulsion breaking chemicals to resolve water-in-oil emulsions is highly parent oil/surfactant specific. The results are strictly valid only for the combinations of demulsifiers (Alcopol O 70% PG, aka Drimax, and Unichem RNB-60425) and emulsions used (50% salt water in either a blend of 80% Hydrocal 300/5% IFO 380/15% diesel, or fresh Endicott crude). The following summarizes the key findings.

Primary Break

In most cases, primary break was achieved in 30 minutes or less (Figure 13). This is entirely consistent with the results of both previous decanting test series at Ohmsett (SL Ross 1999 and 2002).

Partitioning of the Demulsifiers

It was not possible to discern any trends in the partitioning of the demulsifiers between the decanted water and the oily phase due to the limitations of the analytical technique. The same general observations as were noted in the lab-scale tests were evident in the results from the Ohmsett tests, namely:

Table 2: Summary of Ohmsett demulsifier fate test results

Test No.	Oil	Wave No.	Total fluid Flow rate (gpm)	Free Water (avg %)	Demulsifier	Demulsifier Concentration (ppm)	Recovered Emulsion Water Content (avg %)	Emulsion Dehydration (%)			
								2 min.	10 min.	30 min.	60 min.
1	Hydrocal 80/5/15	1	67	12	None	0	No Sample	No Sample	No Sample	No Sample	No Sample
2	Hydrocal 80/5/15	2	104	19	None	0	60	0	0	0	0
3	Hydrocal 80/5/15	1	97	44	Alcopol	1413	16	78	90	44	58
4	Hydrocal 80/5/15	2	80	45	Alcopol	1194	29	44	48	42	36
5	Hydrocal 80/5/15	1	117	16	Alcopol	888	24	54	50	38	64
6	Hydrocal 80/5/15	2	80	49	Alcopol	1354	23	70	62	38	46
7	Hydrocal 80/5/15	1	128	12	Alcopol	0	47	0	0	8	16
8	Hydrocal 80/5/15	2	224	58	Alcopol	425	19	62	58	62	64
9	Endicott	1	135	18	Unichem	1380	34	26	30	32	44
10	Endicott	2	95	34	Unichem	1647	35	42	28	30	20

Test No.	Concentration of Oil in Decanted Water (ppm)				Concentration of Demulsifier In Decanted Water (ppm)			
	2 min.	10 min.	30 min.	60 min.	2 min.	10 min.	30 min.	60 min.
1	No Sample	212	206	918	No Sample	No Sample	2	2
2	No Sample	No Sample	No Sample	No Sample	No Sample	No Sample	No Sample	No Sample
3	8252	1325	1102	452	257	291	401	257
4	3491	799	430	979	445	267	267	257
5	2189	25330	740	22209	140	592	229	401
6	22547	2816	14572	923	630	470	401	445
7	803	506	344	647	33	21	22	15
8	4649	1680	990	1249	279	317	279	364
9	11239	3338	1347	934	241	223	175	171
10	4515	4184	2143	491	301	149	175	156

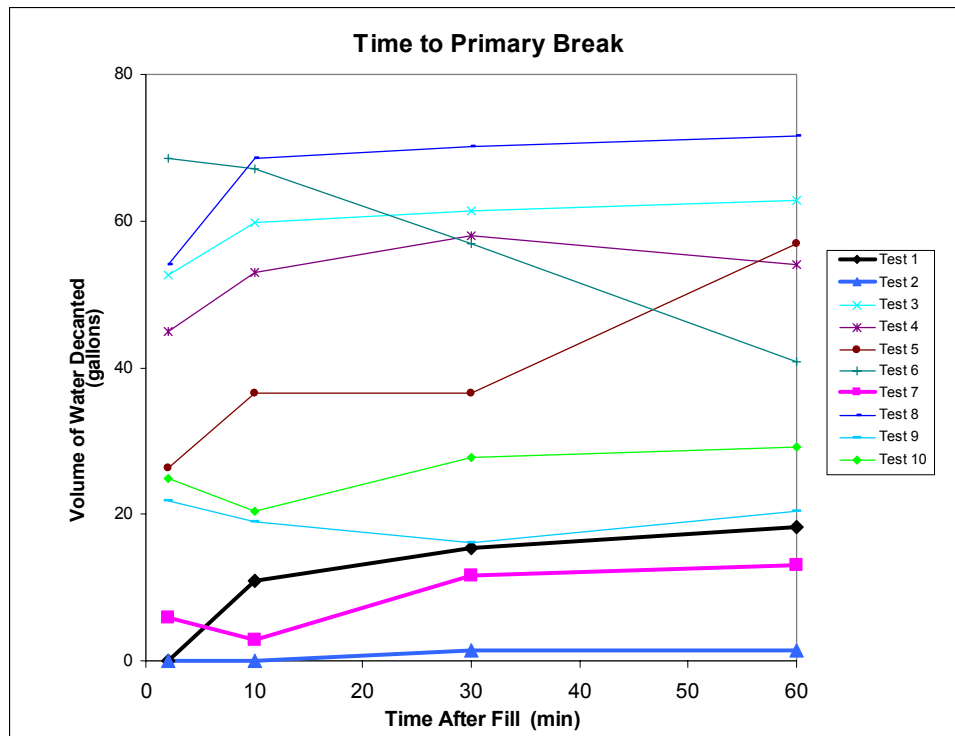


Figure 13: Separation of recovered fluid as a function of time.

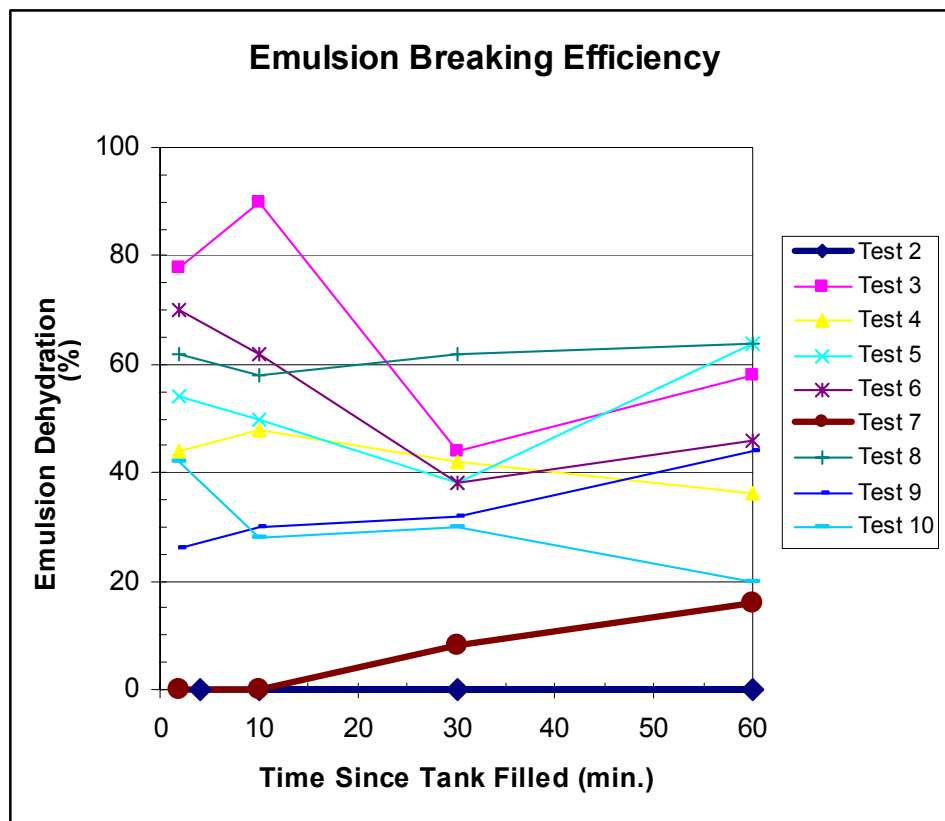


Figure 14. Emulsion breaking efficiency test results.

- A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
- The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as in the 1000's of ppm.

Effectiveness of the Two Demulsifiers in Breaking Emulsions of the Two Oils

The results are presented in Table 2 and Figure 14. Without the addition of demulsifier, there was no dehydration in the emulsions recovered in Wave 1 conditions (length = 11.3 m, $H^{1/3} = 42$ cm), and an increase in the water content of the untreated emulsions (from 50% at 2 min. to 65% at 60 minutes) in the steeper Wave 2 conditions (length = 4.6 m, $H^{1/3} = 38$ cm). The extra mixing energy added to the slick by the steeper Wave 2 conditions caused additional emulsification of the oil (as observed in the previous tests – SL Ross 2002).

The addition of demulsifier caused significant amounts of water to separate from the treated emulsions. In Wave 1 conditions almost $\frac{2}{3}$ rds of the emulsion water was removed and decanted; in Wave 2 conditions, a lesser degree of emulsion dehydration was calculated; however, these calculations are based on the assumption that the emulsion has an initial water content of 50%. If, as is likely, the emulsion water content was upwards of 65% by the end of a test in Wave 2 conditions, the dehydration efficiencies would be closer to 60%, rather than 36% and 46%. The best dehydration obtained was for a run in Wave 2 with the lowest dose rate of Alcopol of all, but with a recovery rate almost twice that of any other test. The 60-minute dehydration result of 64% (72%, if a 65% water content emulsion was being skimmed) was a testament to the fact that mixing energy is very important for effective emulsion breaking, even more so than demulsifier dose rate. The results obtained at Ohmsett were consistent with those from the lab tests with free water contents of less than 50%.

The efficiency of the Unichem demulsifier on the emulsions of fresh Endicott crude was not as high as the Alcopol with the Hydrocal blend emulsions, but the results were encouraging nonetheless. This is because the demulsifier is not an oil spill demulsifier, but a product designed for oil field production purposes (and hence, stored in large quantities in Alaska at the oil fields). In Wave 1 conditions, 44% dehydration was achieved in the 60-minute sample. In Wave 2, 20% dehydration was calculated after 60 minutes (40%, if the emulsion was 65% water, not 50%).

Oil Content of the Decanted Water

In general, the concentration of oil in the decanted water (Table 2) declined from values in the thousands of ppm after two minutes, to the high hundreds of ppm after 60 minutes. The baseline results were generally similar to those obtained in the previous test series, with Total Petroleum Hydrocarbon (TPH) values determined by gas chromatography in the 200 to 1000 ppm range. The TPH values measured with tests involving demulsifier on Hydrocal blend emulsions were general higher than those obtained in the previous demulsifier test series. This was likely due to the addition of 15% diesel to the parent oil blend for the present test series. This would make the parent oil significantly less viscous,

and hence easier to shear into very small droplets that take longer to rise out of the water. The TPH results for the Endicott emulsions treated with the Unichem demulsifier were in the same range as the results for the Hydrocal emulsion treated with the Alcopol demulsifier.

2.5 Summary of All Experimental Results

- “Primary break” (the initial separation of the recovered fluid into a layer containing most of the oil and a layer containing most of the free water) occurs within a few minutes to one hour, depending of the physical characteristics of the oil.
- Rapidly decanting this free water layer, in appropriate situations, may offer immediate increases of 200 to 300% in available temporary storage space.
- Initial TPH concentrations in the decanted water also depended on the physical properties of the oil; they ranged from 100 to 450 mg/L for the most viscous oil to 1400 to 3000 mg/L for the least viscous. These declined by a factor of approximately 3 after one hour of settling, and by a factor of approximately 5 after one day.
- The use of a demulsifier injected into a recovery system, combined with decanting, substantially reduced the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.
- The application of demulsifier did not appear to affect the time required to achieve “primary break”.
- The efficacy of the demulsifier was a strong function of free water content. In these tests, if the free water content exceeded about 55%, the effect of the surfactant was substantially reduced.
- The degree of emulsion breaking achieved increased with increasing mixing energy applied to the recovered fluids. Increasing the flow rate (and hence turbulence level), adding mechanical mixing energy and increasing the length of the flow path all resulted in increased emulsion breaking.
- The Ohmsett results indicated that the use of a demulsifier approximately doubled TPH concentrations in the decanted water.
- The formation of micelles by the demulsifier surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure the concentration of the demulsifiers in the decanted water make definitive conclusions about the partitioning of the demulsifier between oily and water phases impossible. The following general conclusions could be made:
 1. A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
 2. The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as in the 1000’s of ppm.

The major implication of this research for oil spill response is that it may be possible to greatly reduce downtime for offshore skimming operations caused when the available onsite temporary storage systems are filled with fluids containing large amounts of water; however, it is likely that much of the demulsifier used will be contained in the decanted

water. Knowing that the separated water can be decanted quickly will optimize onsite recovery operations and greatly reduce the volume of fluids requiring disposal. In fact, the removal of most of the free and emulsified water from the recovered product would greatly enhance the likelihood that it could be recycled, as opposed to requiring disposal.

3. REGULATORY REGIME GOVERNING DECANTING

This section reviews and summarizes the regulations and guidance governing decanting at the international, national, regional and local level. The purpose is to identify the specific concerns of the rule makers regarding environmental and operational issues regarding decanting, specific guidance offered to address these concerns and quantitative data and analyses upon which the guidance was based. The national spill plans (e.g., NCP (U.S.), agency plans (Canada)), regional plans (e.g., Regional Environmental Emergency Team (Canada)) and local plans (e.g., ACPs (U.S.)) were reviewed. Guidance and restrictions on decanting were summarized.

The overarching regulations can be summarized as follows:

3.1 International Waters

The discharge of oil by vessels into the sea is prohibited under MARPOL 73/78, with the following exceptions:

- The oil content of the discharge does not exceed 15 ppm (except in Special Areas, such as the Antarctic or the Great Lakes, where no oil content is permitted);
- "...the discharge into the sea of substances containing oil, approved by the Administration, when being used for the purpose of combating specific pollution incidents in order to minimize the damage from pollution. Any such discharge shall be subject to the approval of any Government in whose jurisdiction it is contemplated the discharge will occur."

3.2 U.S. Federal Waters

The United States Federal On Scene Coordinator (FOSC) is granted an exclusion from the National Pollutant Discharge Elimination System (NPDES) permit requirement for discharges under 40 CFR 122.3(d) which states, "Any discharge in compliance with instructions of an On-Scene Coordinator pursuant to 40 CFR 300 (The National Oil and Hazardous Substances Pollution Contingency Plan) or 33 CFR 153.10(e) (Pollution by Oil and Hazardous Materials)"

Most Area Contingency Plans have detailed instructions on the USCG policy regarding decanting and many contain sample forms for requesting permission to decant from various State and other authorities. The exception seems to be the Great Lakes, in which decanting does not appear to be encouraged. The text in Section 4000 (Planning) of the Maine and New Hampshire ACP is typical:

"4760 Decanting - When oil is spilled on the water, mechanical recovery of the oil is the principal approved method of responding. However, the mechanical recovery process and associated systems necessarily involve placing vessels and machinery in a floating oil environment."

Incidental returns of oil into the response area, such as oil that falls back into the recovery area from vessels and machinery that are immersed and working in the oil, are an inevitable part of the mechanical recovery process. Similarly, separation or "decanting" of water from recovered oil and return of excess water into the response area can be vital to the efficient mechanical recovery of spilled oil because it allows maximum use of limited storage capacity, thereby increasing recovery operations.

This practice is currently recognized as a necessary and routine part of response operations. (See National Contingency Plan Revisions, 59 F.R. 47401, Sept. 15, 1994.) In addition, some activities, such as those associated with oil recovery vessels, small boats and equipment cleaning operations, may result in incidental discharges. These activities may be necessary to facilitate response operations on a continuing basis, and all of these activities are considered to be "incidental discharges."

"4761 Policy - This policy addresses "incidental discharges" associated with spill response activities. "Incidental discharge" means the release of oil and/or oily water within the response area in or proximate to the area in which oil recovery activities are taking place during and attendant to oil spill response activities. Incidental discharges include, but are not limited to, the decanting of oily water, oil and oily water returns associated with runoff from vessels and equipment operating in an oiled environment and the wash down of vessels, facilities and equipment used in the response. "Incidental discharges" as addressed by this policy, do not require additional permits and do not constitute a prohibited discharge. See 33 CFR 153.301, 40 CFR 300."

"4762 Criteria -During spill response operations, mechanical recovery of oil is often restricted by a number of factors, including the recovery system's oil/water recovery rate, the type of recovery system employed and the amount of tank space available on the recovery unit to hold recovered oil/water mixtures. In addition, the longer oil remains on or in the water, the more it mixes to form an emulsified mousse or highly mixed oil/water liquid, which sometimes contains as much as 70% water and 30% oil, thus consuming significantly more storage space. Decanting is the process of draining off recovered water from portable tanks, internal tanks, collection wells or other storage containers to increase the available storage capacity of recovered oil. When decanting is conducted properly most of the petroleum can be removed from the water.

The overriding goal of mechanical recovery is the expeditious recovery of oil from water. In many cases, the separation of oil and water and discharge of excess water is necessary for skimming operations to be effective in maximizing the amount of oil recovered and in minimizing overall environmental damages. Such actions should be considered and in appropriate circumstances authorized by the FOSC and/or SOSC because the discharged water will be much less harmful to the environment than allowing the oil to remain on the water and be subject to spreading and weathering.

During a response, it will likely be necessary for response contractors or a responsible party to request from the FOSC and/or SOSC authority to decant while recovering oil so that response operations do not cease or become impaired. Expeditious review and

approval, as appropriate, of such requests is necessary to ensure a rapid and efficient recovery operation. In addition, such incidental discharges associated with mechanical recovery operations should not be considered prohibited discharges. Therefore, the Area Committee adopts this policy to provide for an expeditious approval process and provide guidance to OSCs, responsible parties, response contractors and other members of the spill response community relating to incidental discharges and decanting.

The Federal and State OSCs will consider each request for decanting on a case by case basis. Prior to approving decanting, the OSCs should evaluate the potential effects of weather including the wind and wave conditions, the quantity of oil spilled and the type of oil as well as available storage receptacles. The OSC should also take into account that recovery operations as enhanced by decanting will actually reduce the overall quantity of pollutants in a more timely and effective manner to facilitate cleanup operations.

The following criteria should be considered by the FOSC and/or SOSC in determining whether to approve decanting unless circumstances dictate otherwise:

- All decanting should be done in a designated "Response Area" within a collection area, vessel collection well, recovery belt, weir area, or directly in front of a recovery system.*
- Vessels employing sweep booms with recovery pumps in the apex of the boom should decant forward of the recovery pump.*
- All vessels, motor vehicles and other equipment not equipped with an oil/water separator should allow retention time for oil held in internal or portable tanks before decanting commences.*
- When deemed necessary by the FOSC and/or SOSC or the response contractor a containment boom will be deployed around the collection area to minimize loss of decanted oil or entrainment.*
- Visual monitoring of the decanting area shall be maintained so that discharge of oil in the decanted water is detected promptly.*
- Decanting in areas where vacuum trucks, portable tanks or other collection systems are used for shore cleanup will be subject to the same rules as vessels.*

The response contractor or responsible party will seek approval from the FOSC and/or SOSC prior to decanting by presenting the Unified Command with a brief description of the area for which decanting approval is sought, the decanting process proposed, the prevailing conditions (wind, weather, etc.) and protective measures proposed to be implemented. The FOSC and/or SOSC will review such requests promptly and render a decision as quickly as possible. FOSC authorization is required in all cases and in addition SOSC authorization is required for decanting activities in state waters. The FOSC and/or SOSC will review and provide directions and authorization as appropriate to requests to wash down vessels, facilities and equipment to facilitate response activities”.

It is worth noting that it appears that the Northwest ACP has been recently modified (Change 6) to permit decanting without prior approval during the first 24 hours following a spill.

As well, the decanting policy in the Northwest ACP was submitted to the National Marine Fisheries Service to determine if it contravened the Endangered Species Act or the Magnuson-Stevens Fishery Conservation and Management Act. In order not to contravene these acts the USCG and EPA must implement “Reasonable and Prudent Measures” to minimize and avoid effects, which in the case of decanting are:

1. Location. *Decanting shall be done in designated “response areas” within a collection area, vessel collection well, recovery belt or directly in front of a recovery system.*
2. Vessel Location. *Vessels employing sweep booms with recovery pumps in the apex of the boom should decant forward of the recovery pump.*
3. Retention Time. *Vessels, motor vehicles, and other equipment not equipped with an oil/water separator shall allow sufficient time for oil held in internal or portable tanks before decanting commences.*
4. Containment Boom. *A containment boom will be deployed at the collection area to minimize loss of inadvertently decanted oil into the environment whenever possible.*
5. Monitoring. *Visual monitoring of the decanting area shall be maintained so that discharge of oil in the decanted water is detected promptly and operations shut down.*
6. Non-vessel Decanting. *Decanting in areas where vacuum trucks, portable tanks or other collection systems are used for shore cleanup will be subject to the same rules as vessels.*

3.3 State Waters

Although each State has its own regulations, and some States may prohibit decanting (such as in the Great Lakes) New Hampshire’s regulations appear to be typical:

“Decanting oily water from barges or vessels to provide volume for free-phase oil is extremely important during response efforts. Mechanical skimming devices are not very efficient. They pick up large percentages of water along with the oil. In order to maximize recovery capability, it is necessary that excess water be discharged back into the contaminated area during the collection phase”.

“The Clean Water Act (CWA) provides for emergency situations such as this, by authorizing the On-Scene Coordinator to grant permission for such a discharge (see 40 CFR 122.3[d]):

40 CFR Sec. 122.3 Exclusions.

The following discharges do not require NPDES permits:

(d) Any discharge in compliance with the instructions of an On-Scene

Coordinator pursuant to 40 CFR part 300 (The National Oil and Hazardous Substances Pollution Contingency Plan) or 33 CFR 153.10(e) (Pollution by Oil and Hazardous Substances).

Similarly, RSA 485-A:16 contains the State of New Hampshire provision for emergency discharges:

NH RSA 485-A:16 Emergency

If the (Water) division finds that an emergency has arisen from the failure of or casualty to facilities for the control of pollution, the division may, if it finds that the best interests of the public will not unduly suffer, authorize any person for a reasonable periods of time to discharge sewage or other wastes into surface waters or ground waters, although such discharge would have the effect of lowering the quality of such waters below the adopted classification. Clarification of this provision in regards to petroleum products can be found in the definition section of RSA 485:

NH RSA 485-A:2 (VIII) Definitions

“Other wastes” means garbage, municipal refuse, decayed wood, sawdust, shavings, bark, lime, ashes, offal, oil, tar, chemicals and other substances other than sewage or industrial wastes, and any other substance harmful to human, animal, fish or aquatic life.

3.4 Canadian Waters

Section 678.2 (1) of the Canada Shipping Act offers protection to any certified response organization or its employees “decanting” in the course of oil spill cleanup. Protection against liability is removed only when the “conduct was not reasonable in the circumstances” and, in these cases, there would be a liability under the Fisheries Act (pollution of fish habitat) or under the Canadian Environmental Protection Act (ocean dumping). Note: It is considered reasonable to expect decanted water to be discharged in front of the skimmer operation.

3.5 Summary

Although the above summary demonstrates that the statutory instruments appear to be in place to permit decanting, and that it should take place in front of the recovery operations, it is also apparent that there is very little guidance available to the FOSC or SOSC on the likely concentrations of oil in decanted water, appropriate environments in which to permit decanting and the implications of demulsifier use on the advisability of decanting. Only NOAA, in their History and Status of Applied Technologies web site mentions the use of demulsifiers to aid decanting, and only broadly addresses the issues:

“The latest proposed use of emulsion breakers is injection of the agent into the emulsion early in the recovery process while at sea, such as in the containment boom, skimmer pump, skimmer reservoir, settling tank, or storage barge. Injection at the skimmer pump head could improve pumping as well as increase mixing and subsequent separation of the water. The objective is to decrease the on-scene storage requirements for recovered oil. There are commercially available skimmers with injection systems capable of using emulsion-treating agents. Breaking of emulsions and decanting of the released water in

skimmers could be extremely important during large spills, since storage of recovered product can be a limiting factor in the rate of oil recovery. A high-volume skimmer (e.g., GT-185 or DESMI) can exceed its on-board storage capacity for recovered product within the first few hours of operations. Operationally, the critical issue is the time needed to break the emulsion in the skimmer, which should be accomplished within minutes, rather than hours. Environmentally, the critical issue is whether regulatory agencies would allow the discharge of the released water back into the sea without treatment. Specific permits may be required if the water contains regulated chemicals.”

The next two sections of this report address these issues.

4. SCENARIOS REGARDING THE POTENTIAL BENEFIT OF DECANTING AND EMULSION BREAKING

The following section describes the potential benefits of decanting and emulsion breaking when applied to a spill response involving conventional containment and recovery techniques. The fluid-handling aspects of the spill response are described in quantitative terms, first using a typical response module involving containment boom, a high-rate skimmer, and a series of sea-going barges to store recovered fluids, then second using the guidelines for response organizations listed in CFR 155.

4.1 Response with a High-Rate Skimming Unit

Consider first a containment and recovery system comprising 1000 feet of boom, one high-rate weir-type skimmer, a barge to receive collected fluids, and supporting vessels. Soon after the spill, the oil emulsifies to form a 75% water-in-oil emulsion (75% water, 25% oil). In the first few days of the spill, while the slick is thick and coherent, the system should be able to encounter thick patches of oil averaging 1 mm or more in thickness, so the encounter rates of the system should be in the range of 800 bbl/h (130 m³/h). Weir skimmers are available with this capacity (and more), so we can use this number as the emulsion recovery rate. At such rates, weir skimmers typically recover a mixture of 50% emulsion and 50% water (Nordvik 1989), so the total fluid recovery rate is 1,600 bbl/h. A typical barge used to support such an operation would have a capacity of 8,000 barrels: in five hours, the barge would be filled. Its contents would be:

- 4,000 barrels of emulsion, containing
 - 1,000 barrels of oil, and
 - 3,000 barrels of water contained in the emulsion
- 4,000 barrels of free water

At this point, a second barge would be required, the first one being taken out of service and shuttled to an offloading location. An estimate of the offloading time would be 20 hours; comprising 12 hours return transit (30 miles each way ÷ 5 knots), and 8 hours offloading time (8,000 barrels ÷ 1,000 bbl/h).

Decant and Discharge Free Water

Now consider the potential benefits of decanting free water from the storage barge during the recovery operation. If the decanting operation can proceed while skimming is ongoing, then the effective fluid recovery rate is only half the 1,600 bbl/h, or 800 bbl/h, and the barge could remain on-scene and in operation for 10 hours. (Note that this would require that the barge would have a number of segregated tanks; while one is receiving fluids from the skimmer, another would be decanted of free water to gain additional storage space. This will be assumed to be the case for this simplified example.) In this situation, in the first five hours, no decanted water would be discharged and in the second five hours all the 8,000 bbls of free water would be discharged at a rate of 1,600 bbls/hr (or 1,120 gpm = 70 L/s). The concentration of oil droplets in this water would likely be in the 500 to 1,000 ppm range for light oils and in the 50 to 200 ppm range for heavier oils and emulsions.

Inject Demulsifier, Decant Emulsion Water and Discharge with Free Water

If the recovered emulsion can be treated with emulsion-breaker, additional water can be decanted and offloaded. A reasonable estimate of emulsion-breaker effectiveness is that a 75% emulsion can be quickly reduced to a 25% emulsion, so the 4000 barrels of emulsion can be converted from a mixture of 1,000 barrels oil and 3,000 barrels water, to a mixture of 1,000 barrels oil and 333 barrels water, effectively liberating 2,667 barrels of previously emulsified water. If this could also be decanted and offloaded, the effective fluid recovery rate would then be 267 bbl/h (instead of 200 bbl/h oil and 600 bbl/h emulsified water, the 75% emulsion, 200 bbl/h oil and 67 bbl/h emulsified water, a 25% emulsion). Again simplifying the example to assume that emulsion breaking, decanting, and offloading of water, the barge would not be filled for 30 hours ($8000 / 267$). In this case the system would recover a total of 24,000 bbls of free water and 24,000 bbls of emulsion over 30 hours, of which 24,000 bbls of free water and 16,000 bbls of emulsion water would be decanted and discharged. Assuming that no discharge of water occurs in the first five hours, the average rate of water discharge would be $([24,000 + 16,000]/25) = 1,600$ bbls/hr (or 1120 gpm = 70 L/s). The concentration of oil droplets in this water would likely be in the 1,000 to 2,000 ppm range for lighter parent oils and in the 100 to 400 ppm range for heavier parent oils. The concentration of demulsifier surfactants in the water would be in the range of 200 to 1,000 ppm. If the recovered fluid stream was treated with demulsifier at a dose rate of 1:1000 the total amount of demulsifier injected over the 30-hour recovery period would be 48 bbls and the concentration of demulsifier in the discharged water would be at most $(48/[24,000 + 16,000 + 2,000])$ approximately 1,100 ppm.

The comparison of the three options can also be put into terms of the number of barges required to support this unit operation. The following assumes a 12-hour day in which skimming operations would be conducted, a 24-hour day for conducting the barge shuttle and offloading operation, and only looks at the first three days when skimming operations would not be limited by encounter rate considerations as the slick thins and spreads out. In the first example, with no decanting or emulsion breaking, three barges would be required on Day 1. On Days 2 and 3, no additional barges would be required as long as the shuttle-offloading operation could proceed as described, and as barges are emptied they are promptly returned to service. With decanting alone, three barges would also be required, but the third barge would not be required until the second day of skimming operations. Finally, with decanting and emulsion breaking, only two barges would be needed, with the second one not being required until the third day of the response, a considerable advantage in logistics.

4.2 Response Using OSRO Guidelines

Guidelines for required response resources for Vessel Response Plans are contained in 33 CFR 155, Appendix B (www.uscg.mil/vrp/reg/33cfr155appb.shtml). For the immediate response to large spills, it is appropriate to look at the “caps”, or maximum required values, for a Tier 1 response. The required capability for a Tier 1 response is “capped” at 12,500 bbls/day recovery capacity, with double that amount, 25,000 bbls/day required for storage. (The regulations suggest the assumption that the recovery efficiency would be

50%, that equal amounts of free water and oil or emulsion would be recovered.) That would equate to slightly more than three of the 8,000-barrel barges used in the above analysis. Using the same logic as above, three additional barges would be required on the second day of the response.

Decant and Discharge Free Water

If decanting of free water were an option, the barge requirement could be cut essentially in half, with only two barges required on Day 1, and a third on Day 2. (In both examples, by Day 3, barges from Day 1 would have been returned to service.) In this situation, all the 12,500 bbls of free water each day would be discharged at a rate of 520 bbls/hr (or 365 gpm = 23 L/s). The concentration of oil droplets in this water would likely be in the 500 to 1,000 ppm range for light oils and in the 50 to 200 ppm range for heavier oils and emulsions.

Inject Demulsifier, Decant Emulsion Water and Discharge with Free Water

The regulations also list values for potential emulsification, although these do not change the total recovery or storage volumes needed beyond the “cap” requirements. The regulations do recognize, for planning purposes, that oil may emulsify up to 50% water content in the case of Type 3 oils. The 12,500 bbl/day of recovery capacity could then be considered to include 6,250 bbls of emulsified water, half of which (3,125 bbls) could potentially be removed if an emulsion breaker were able to reduce the emulsion water content to 25%. If this water could also be removed the barge requirement could be lessened further, to only two barges in total, the second only being required late in Day 1. The average rate of water discharge would be $([12,500 + 3,125]/24) = 651$ bbls/hr (or 456 gpm = 29 L/s). The concentration of oil droplets in this water would likely be in the 1000 to 2000 ppm range for lighter parent oils and in the 100 to 400 ppm range for heavier parent oils. The concentration of demulsifier surfactants in the water would be in the range of 200 to 1,000 ppm, depending on the dosage rate. If the recovered fluid stream was treated with demulsifier at a dose rate of 1:1000 the total amount of demulsifier injected in one day would be 25 bbls and the concentration of demulsifier in the discharged water would be at most $(25/[12,500 + 3,125 + 3,125])$ approximately 1,300 ppm.

Table 3 summarizes the rates of water and concentrations of suspended oil droplet and dissolved demulsifier discharged in the various scenarios.

Table 3: Summary of water discharges for various decanting scenarios

Scenario		Average rate of water discharge			Concentration of suspended oil droplets [ppm]		Concentration of dissolved demulsifier [ppm]
		[Bbl/hr]	[gpm]	[L/s]	Lighter oil	Heavier oil or emulsion	
High rate skimmer	Free water	1600	1120	70	500 - 1000	50 – 200	-
	Free and emulsion water	1600	1120	70	1000 - 2000	100 – 400	200 - 1000
OSRO Guidelines	Free water	520	365	23	500 - 1000	50 – 200	-
	Free and emulsion water	650	456	29	1000 - 2000	100 – 400	200 - 1000

4.3 Dilution of Decanted Water Plume

The dilution of the plume of decanted water discharged overboard was modelled using the US E.P.A.'s Visual Plumes computer model (Frick et al. 2001). The assumptions for this exercise were that:

- The water was at least 100 m deep,
- The water temperature was 20°C with a salinity of 31 ppt,
- There was no mixing floor (pycnocline or thermocline) present,
- The discharging vessel was moving ahead at a speed over the water of 0.75 knots,
- The current did not vary with depth,
- The decanted water was discharged through a 6-inch hose, 1 m below the water surface directed at a 45° angle backwards,
- The decanted water discharge rate was either 70 L/s or 30 L/s, and
- The decanted water temperature was 20°C with a salinity of 31 ppt.

Figure 15 shows the horizontal underwater spreading of the two hypothetical plumes of decanted water (1,600 bbl/hr in red and 650 bbl/hr in blue) as they move away from the discharge point. The solid line shows the plume centerlines and the markers (red for the 1,600-bbl/hr-scenario and blue for the 650-bbl/hr-scenario) delineate the boundaries of the plume as defined by a 3/2-power model of plume diffusion. Note that the x-axis is greatly exaggerated compared to the y-axis. Within 5,000 m of the release point (about 3.5 hours after release), the 1,600 bbl/hr plume is predicted to spread to a width of approximately 40 m and the 650 bbl/hr plume is predicted to spread to a width of approximately 20 m.

Figure 16 shows the downward spreading of the underwater plumes for the same scenarios. Again, the x-axis is greatly exaggerated. The centerline of the 1,600-bbl/hr-scenario plume is predicted to descend to a depth of approximately 27 m 5,000 m after being discharged, with the plume boundaries extending from 8 m deep to 50 m deep. The centerline of the 650-bbl/hr-scenario plume is predicted to descend to a depth of approximately 15 m 5,000 m after being discharged, with the plume boundaries extending from 5 m deep to 25 m deep.

Figure 17 illustrates the predicted dilution of the two hypothetical plumes as they diffuse in the water column. The solid line shows the predicted dilution of the plume average concentration and the markers (red for the 1,600-bbl/hr-scenario and blue for the 650-bbl/hr-scenario) shows the predicted dilution of the plume centerline concentrations as defined by a 3/2-power model of plume diffusion. Within 500 m of release (about 20 minutes at 0.75 knots) the average plume concentration for the 1,600-bbl/hr scenario is predicted to be reduced by a factor of over 1000 and the average plume concentration for the 650-bbl/hr scenario is predicted to be reduced by a factor of approximately 1000. At 500 m, the centerline plume concentrations are predicted to be reduced by factors of approximately 250 and 350 for the 650 and 1,600-bbl/hr scenarios respectively. The centerline concentrations are predicted to be reduced by a factor of 1000 within 2500 and 3500 m.

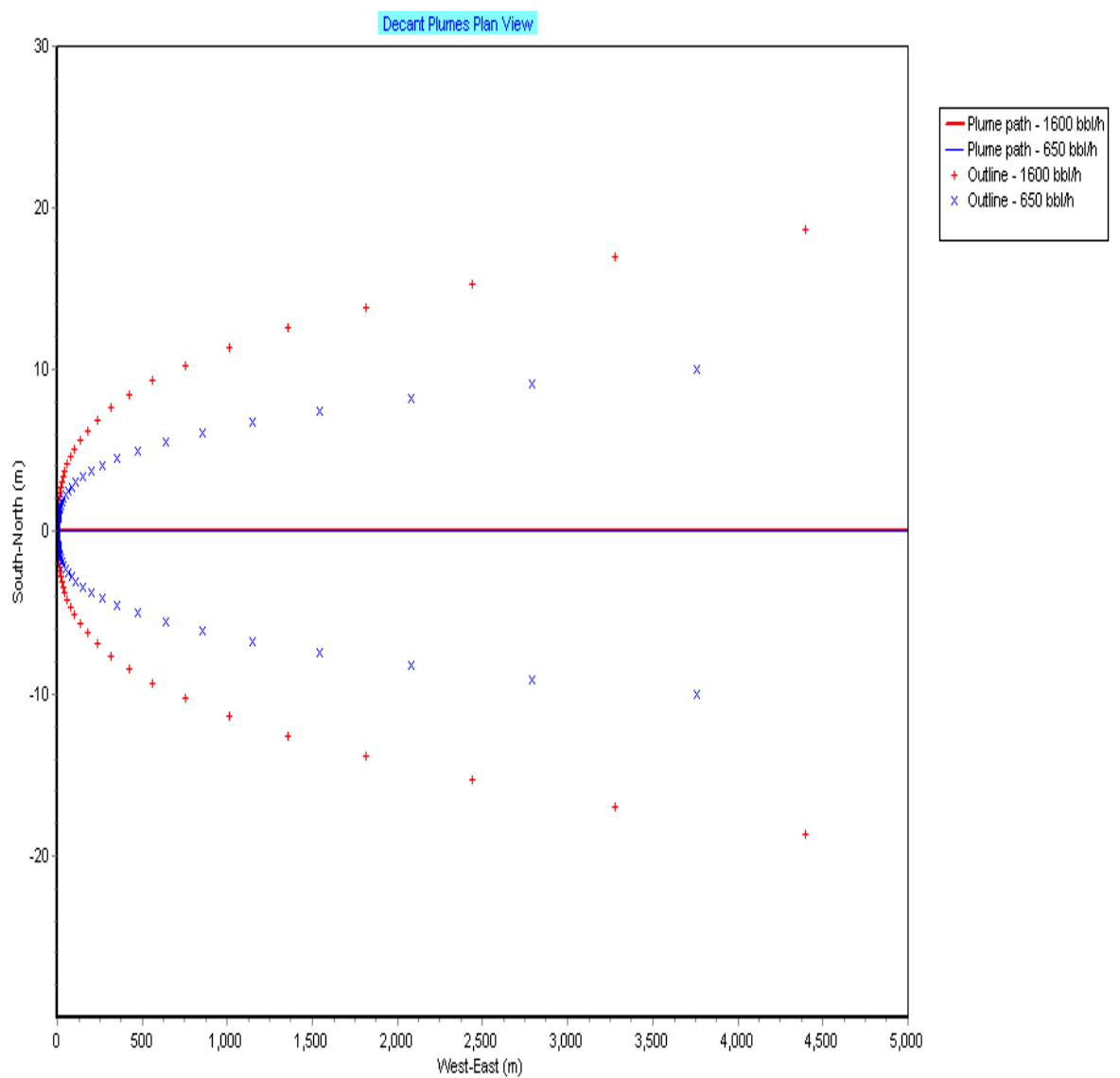


Figure 15: Predicted Horizontal Spreading of Hypothesized Plumes of Decanted Water

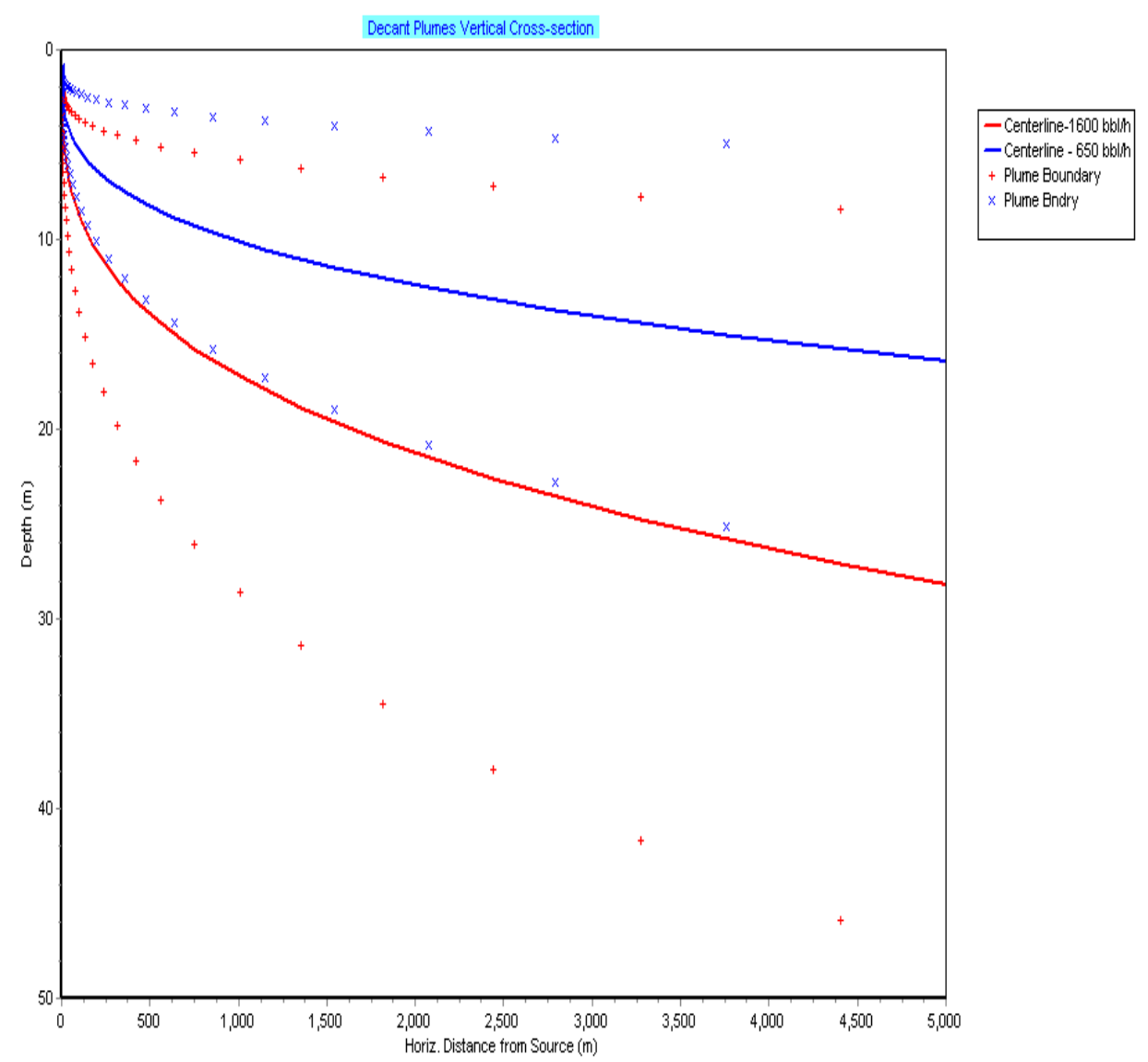


Figure 16. Predicted Downward Spreading of Hypothesized Plumes of Decanted Water

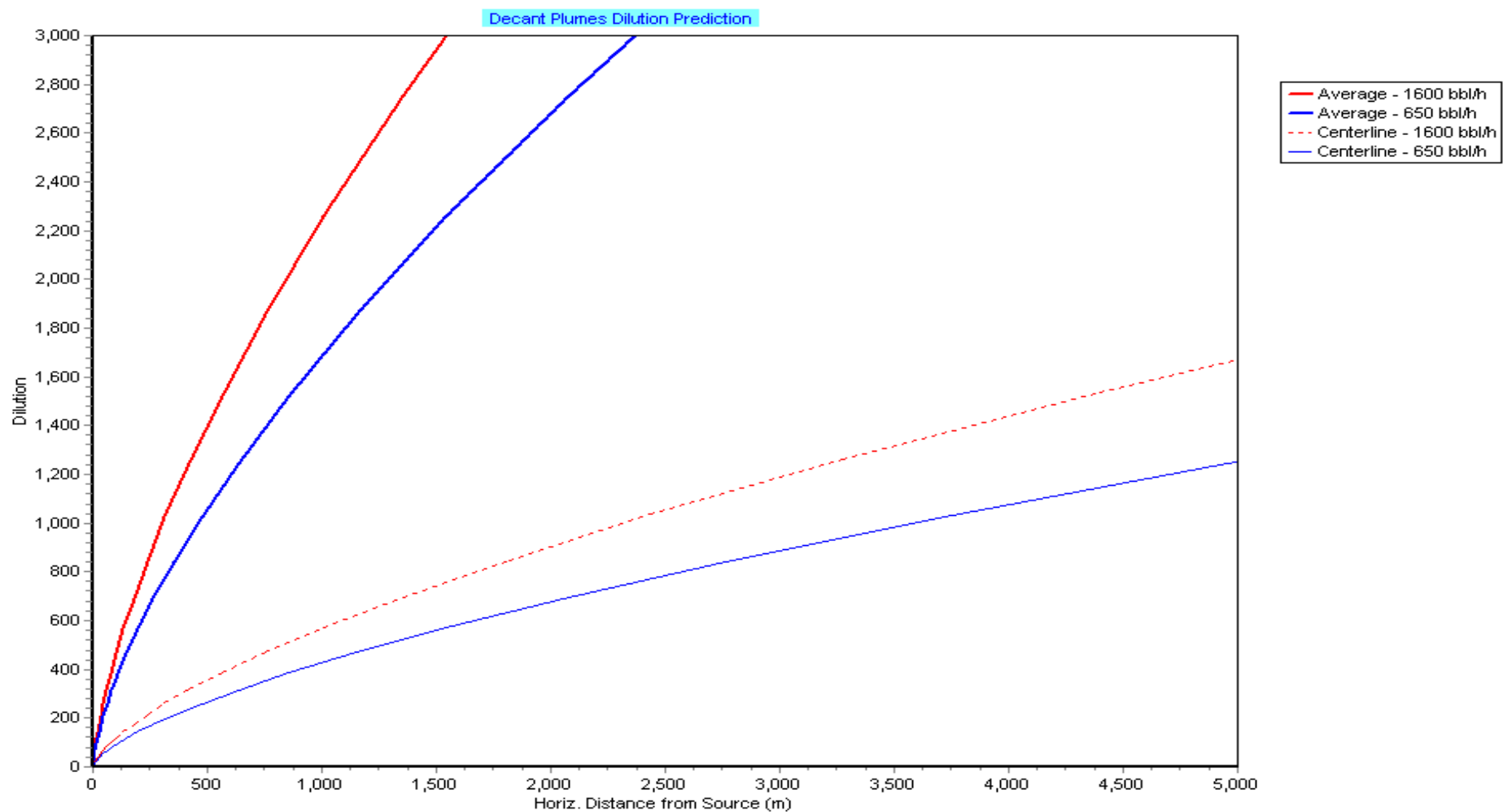


Figure 17. Predicted Dilution of the Centerline and Average Plume Concentrations for the Hypothesized Scenarios.

5. POTENTIAL ENVIRONMENTAL RISKS FROM DECANTING

The following section estimates the potential impact on in-water communities from decanting and discharging the water produced in the fluid-handling scenarios described above. Environmental concerns associated with decanting relate to impact of toxic contaminants in the effluent, principally oil-derived hydrocarbons and demulsifier-derived surfactants. Analyses conducted here evaluate these impacts by assessing:

- a) Whether concentrations of contaminants in the discharged water exceed the toxic threshold for the respective toxicants;
- b) Size of impact footprints created in the upper water column by the plume of decant effluent; and,
- c) The depth to which potentially toxic conditions penetrate into the water column under different operating scenarios.

During skimming/decanting operations, an operational unit moves, collecting oil and discharging decanted water generating an effluent plume. The effluent, which contains identified concentrations of toxicants, is discharged at hypothesized rates at a depth of one metre below the sea surface as the vessel proceeds at a given speed for the duration of the skimming operation. The jet of decanted water exiting the discharge hose mixes immediately with the surrounding water and the resulting plume spreads horizontally and vertically in the water column by turbulent diffusion, as described in the previous section.

Obviously, toxicant concentrations are greatest in the effluent as it is discharged, but as the plume spreads, toxicant concentrations decline quickly through dilution. Though toxicant concentrations in the effluent may exceed toxic levels initially, these concentrations decline quickly with time through dilution, falling below toxic levels and ultimately declining to background levels. This section estimates both the effective plume width and effective plume depth at the point at which contaminant concentrations in the plume reach the thresholds for acute lethality for each toxicant (petroleum hydrocarbons and demulsifier). The product of the plume width and the distance travelled during the skimming/decanting operation yield the size of the toxic footprint of the operation in the upper water column. The depth to which the plume penetrates while continuing to be toxic is an indicator of the potential risk to the seabed community.

5.1 Toxicity of Plume Contents

Toxic potency of the two critical effluent components was established from published data. Toxicities of demulsifiers and aqueous extracts of crude oil vary widely depending on the type or source of toxicant involved (i.e. type of crude oil and demulsifier), biological species tested, exposure conditions and toxic endpoint. An exhaustive treatment of the toxicology of these factors is beyond the scope of this project. Rather for the purpose of this work, approximate and conservative toxicity thresholds were assumed based on published data, as follows.

The toxic threshold for the petroleum hydrocarbon component was based on the 96HRLC50 values for toxicity of water-accommodated fractions (WAF) of various crude

oils to various marine species during continuous exposure (Table 4). Using these data a conservative value for the toxic threshold for WAF of crude oil was set at 1 ppm TPH, which was equal to the 75% exceedence value for the data set (i.e., a value selected for which 75% of published values were equal to or greater than this value). The toxic threshold for the demulsifier component was based on the 96HRLC50 values for a range of oil spill demulsifier products to various species during continuous exposure (Table 5). A conservative value for the toxic threshold for demulsifiers was set at 62 ppm demulsifier, which was equal to the lowest toxic threshold value for demulsifiers reported in the literature.

Impact assessment aspects of these operations are described in quantitative terms below using the same “typical response” module and “OSRO guidelines-based” module described in Section 4 above.

5.2 High-Rate Skimming Unit Operating at Capacity

Decant and Discharge Free Water

In this scenario, during each of the first three days of operations, this unit collects oil for 12 hours per day and discharges all 8,000 barrels of collected free water during a 5-hour period each day at a rate of 1,600 bbl/hr. Since no demulsifier was used in this scenario only toxicity of the dissolved and particulate hydrocarbons is considered. These toxicants are present at concentrations ranging from a low of 50 to a high 1,000 ppm TPH depending on the type of oil involved. Environmental risks were scoped using the lowest and highest levels of hydrocarbons likely to be present in the effluent from decanting, namely 50 and 1000 ppm, respectively.

Average TPH concentrations across the width of the plume and at the centerline, as well as plume dimensions are shown as a function of time since discharge in Figure 18. Impact parameters are summarized in Table 6.

When TPH levels in the effluent are at the lower end of the range, 50 ppm, the oil concentrations in the effluent exceed the lethal toxicity threshold at the point of discharge, but modeling results show that concentrations decline to the lethal threshold (=1 ppm) within 0.04 hours (=2.4 minutes) at which time the plume width is approximately 2 m. By discharging effluent for 5 hours per day for three days, this would result in an impact footprint of approximately 0.047 km². By the time the average oil concentrations within the plume decline to toxic threshold levels, the plume will have penetrated to a depth of 10 m. It is important to recognize that oil concentrations in the center of the plume (centerline) remain elevated for somewhat longer, 0.06 hr in this example versus 0.04 hours for the plume average concentrations. By the time the TPH concentrations in the plume centerline have fallen below the toxic level, the plume centerline has penetrated to a depth of only 8 m.

For effluents containing 1000 ppm TPH, the plume would impact a greater area and greater depths. The effective plume width for impact would increase to 6 m and the

impact footprint would be 0.142 km². Toxic conditions would penetrate to depths of 19 m (plume average) and 22 m (plume centerline).

Inject Demulsifier, Decant Emulsion Water and Free Water

If the collected emulsion is broken using a demulsifier and the emulsion water and free water are decanted as described, effluent is discharged at a rate of 1,600 bbl/hr for 57 of the operating hours in the first three days of the cleanup. Toxicant concentrations in the effluent are 100 to 2000 ppm TPH for oil and 1100 ppm for demulsifier. When the TPH content of decanted water is 100 ppm, the average oil concentrations in the plume would be expected to decline to the lethality threshold within 0.05 hours at which time the plume width is approximately 4 m (Figure 19). By discharging effluent for 57 hours over the first three days, this would result in an impact footprint of approximately 0.317 km². Toxic conditions would penetrate to depths of 11 m (plume average) and 9 m (plume centerline). If the decanted water contained 2000 ppm TPH, the effective plume width for impact would increase to 10 m and the impact footprint would be 0.792 km². Toxic conditions would penetrate to depths of 26 m (plume average) and 30 m (plume centerline).

Modeling data suggest that risks from the demulsifier would be much less than from the oil due largely to the demulsifier's lower toxicity (Figure 19). Though demulsifier concentrations exceed toxic threshold values when discharged, they decline to non-toxic levels quickly, with 0.03 hours (1.8 minutes) at which time the plume width is 2 m. The depths to which toxic demulsifier concentrations extend would be 8 m for the plume average and 10 m for the plume centerline. The demulsifier yields a much smaller toxic footprint than the hydrocarbons; hence its contribution to the impact of the decanting operation is modest.

5.3 Response Using OSRO Guidelines

Decant and Discharge Free Water

In operations conducted according to OSRO guidelines, free water is discharged at a rate of 520 bbl/hr for 24 hours each day during the first three days of the cleanup.

Hydrocarbon concentrations in the effluent are 50 to 1000 ppm TPH. When the TPH content of decanted water is 50 ppm, the average plume oil concentrations decline to the lethality threshold within 0.04 hours when the plume width is 2 m (Figure 20). By discharging effluent for 52 hr, this would result in an impact footprint of approximately 0.158 km². Toxic conditions would penetrate to depths of 6 m (plume average) and 5 m (plume centerline). If the decanted water contained 1000 ppm TPH, the effective plume width for impact would increase to 4 m, the impact footprint would be 0.317 km²; and toxic conditions would penetrate to depths of 13 m (plume average) and 14 m (plume centerline).

Inject Demulsifier, Decant Emulsion Water and Free Water

If the emulsion is broken using demulsifier and the emulsion water and free water are decanted, effluent is discharged at a rate of 650 bbl/hr for 57 of the operating hours in the

first three days of the cleanup. Hydrocarbon concentrations in the effluent are 100 to 2000 ppm TPH for oil and 1300 ppm for demulsifier. When the TPH content of decanted water is 100 ppm, the average plume oil concentrations would decline to the lethality threshold within 0.05 hours at which time the plume width is approximately 2 m (Figure 21). By discharging effluent for 57 hours over the first three days, this would result in an impact footprint of approximately 0.158 km². Toxic conditions would penetrate to depths of 6 m (plume average) and 6 m (plume centerline). If the decanted water contained 2000 ppm TPH, the effective plume width for impact would increase to 6 m and the impact footprint would be 0.425 km². Toxic conditions would penetrate to depths of 18 m (plume average) and 22 m (plume centerline). As with the high-rate skimmer operation, modeling data suggest that risks from the demulsifier would be much less than from the oil (Figure 21).

5.4 Summary

In summary, the results of this analysis suggest that the impact of operating a single skimming unit for the first three days of the response operation would be a toxic footprint in the upper water column, ranging in size from 0.04 km² to 0.79 km². The impact derives largely from the impact of the oil. As expected the size of the impact depends on the rate at which oil is collected and the associated water is discharged, but the level of impact can vary by a factor of 2 to 3 depending on the concentration of hydrocarbons in the decanted water.

Table 4: Toxicity of water-accommodated fraction of various crude oils to various marine species

Species (lifestage)	Common Name	Life Stage	Crude Oil Type	96HRLC50 ppm		Spike, ppm		Reference
				Min.	Max.	Min.	Max.	
<i>Pandalus hyposinotus</i>	Coonstripe shrimp	I - VI	Cook Inlet	0.54	7.9			1
<i>Mysidopsis bahia</i>	mysid	10 days old	Arabian Medium	0.56	0.67	26.1	83.1	2
<i>Mysidopsis bahia</i>	mysid	10 days old	Arabian Medium	0.78	0.78	>2.9	>2.9	3
<i>Homarus americanus</i>	American lobster	larvae	Lago Medio	0.8	4.9			4
4 spp	Decapod shrimps	adults	Cook Inlet	1.9	4.3			1
<i>Paralithodes camtschatica</i>	King Crab	larvae	Cook Inlet	2	2			1
<i>Cyprinodon variegatus</i>		3 days old	Arabian Medium	3.9	4.2	5.7	6.1	2
<i>Eualus suckleyi</i>	Kelp shrimp	larvae	Cook Inlet	4.3	4.3			1
<i>Menidia beryline</i>				4.9	5.5	14.5	32.3	2
<i>Capitella capitata</i>				12.5	17.6			5
<i>Capitella capitata</i>				15	19.8			5
<i>Callinectes sapidus</i>	Blue crab	juvenile	Maya	49	49			6
1. Brodersen et al. 1977, 2. Pace et al. 1995, 3. Fuller and Bonner 2003, 4. Wells and Sprague 1977, 5. Rossi and Anderson 1976, 6. Shuba and Heikamp 1987								

Table 5: Summary of information concerning toxicity of emulsion breakers

Product	Species	Common Name	Endpoint	Qualifier	Toxic Threshold, ppm	Ref.
Emulsion Breaker						
Alcopol O 60%	Salmo gairdneri		96HRLC50	>	62	1
Breaker-4	Artemia salina	Brine shrimp	96HRLC50	=	340	1
Brand S Demoussifier	Onchorhynchus mykiss	Rainbow trout	96HRLC50	>	3200	1
Vytac DM	Onchorhynchus mykiss	Rainbow trout	96HRLC50	=	7040	1
Vytac DM	Onchorhynchus mykiss	Rainbow trout	96HRLC50	=	8030	1
Vytac DM	Onchorhynchus mykiss	Rainbow trout	96HRLC50	>	10,000	1
Surfactant						
Diocetyl sodium sulfosuccinate	Onchorhynchus mykiss	Rainbow trout	96HRLC50	=	28	2
1. Environment Canada, Unpublished 2. Goodrich et al 1991.						

Table 6: Summary of impact parameters for all scenarios

Treatment	Discharge Rate, bbl/h	Initial Oil Conc., ppm	Initial Demulsifier Conc., ppm	Plume Average Or Center	Impact of Oil			Impact of Demulsifier			Area of Effect and Depth Penetration	
					Time to Threshold, hours	Effective Plume width	Effective Plume depth	Time to Threshold, hours	Effective Plume width	Effective Plume depth	Impact Footprint ¹ In three Days, km ²	Effective Plume Penetrates Below ² , 10 m
No Decanting	0	0	0		0	0	0	0	0	0	0.000	no
OSRO Guidelines, Free Water Only	520	5050	0	Average Centerline	0.04 0.07	2 -	6 5	na na	na -	na na	0.158 -	no no
OSRO Guidelines, Free Water Only	520	1000	0	Average Centerline	0.3 2	4 -	13 14	na na	na -	na na	0.317 -	yes yes
OSRO Guidelines, With Demulsifier	650	100	1300	Average Centerline	0.05 0.1	2 -	6 6	0.03 0.05	2 -	5 4	0.158 -	no no
OSRO Guidelines, With Demulsifier	650	2000	1300	Average Centerline	0.8 6	6 -	18 22	0.03 0.05	2 -	5 4	0.475 -	yes yes
High Rate Skimmer, Free Water Only	1600	50	0	Average Centerline	0.04 0.06	2 -	10 8	na na	na -	na na	0.047 -	yes no
High Rate Skimmer, Free Water Only	1600	1000	0	Average Centerline	0.2 1.5	6 -	19 22	na na	na -	na na	0.142 -	yes yes
High Rate Skimmer, With Demulsifier	1600	100	1100	Average Centerline	0.05 0.08	4 -	11 9	0.03 0.03	2 -	8 10	0.317 -	yes yes
High Rate Skimmer, With Demulsifier	1600	2000	1100	Average Centerline	0.5 4	10 -	26 30	0.03 0.03	2 -	8 10	0.792	yes yes
1. Effective plume width x distance travelled during decanting operations in 3 operating days = impact footprint in the upper water column. 2. Lower edge or plume centerline penetrates below 10 m while toxicant concentration exceeds toxic threshold for either hydrocarbons or demulsifier.												

Table 7. Summary of Impact Parameters for Hydrocarbon Contaminants

	Effective Plume Width, m		Effective Plume Depth Penetration, m		Area of Toxic Footprint in Upper Water Column, km²	
Discharge Rate, bbl/hr	Low Hydrocarbon Load	High Hydrocarbon Load	Low Hydrocarbon Load	High Hydrocarbon Load	Low Hydrocarbon Load	High Hydrocarbon Load
650	2	4	6(5)	13 (14)	0.042	.083
650	2	6	6(6)	18(22)	0.158	.475
1600	2	6	10 (8)	19 (22)	0.042	.125
1600	4	10	11(9)	26 (30)	0.317	.792

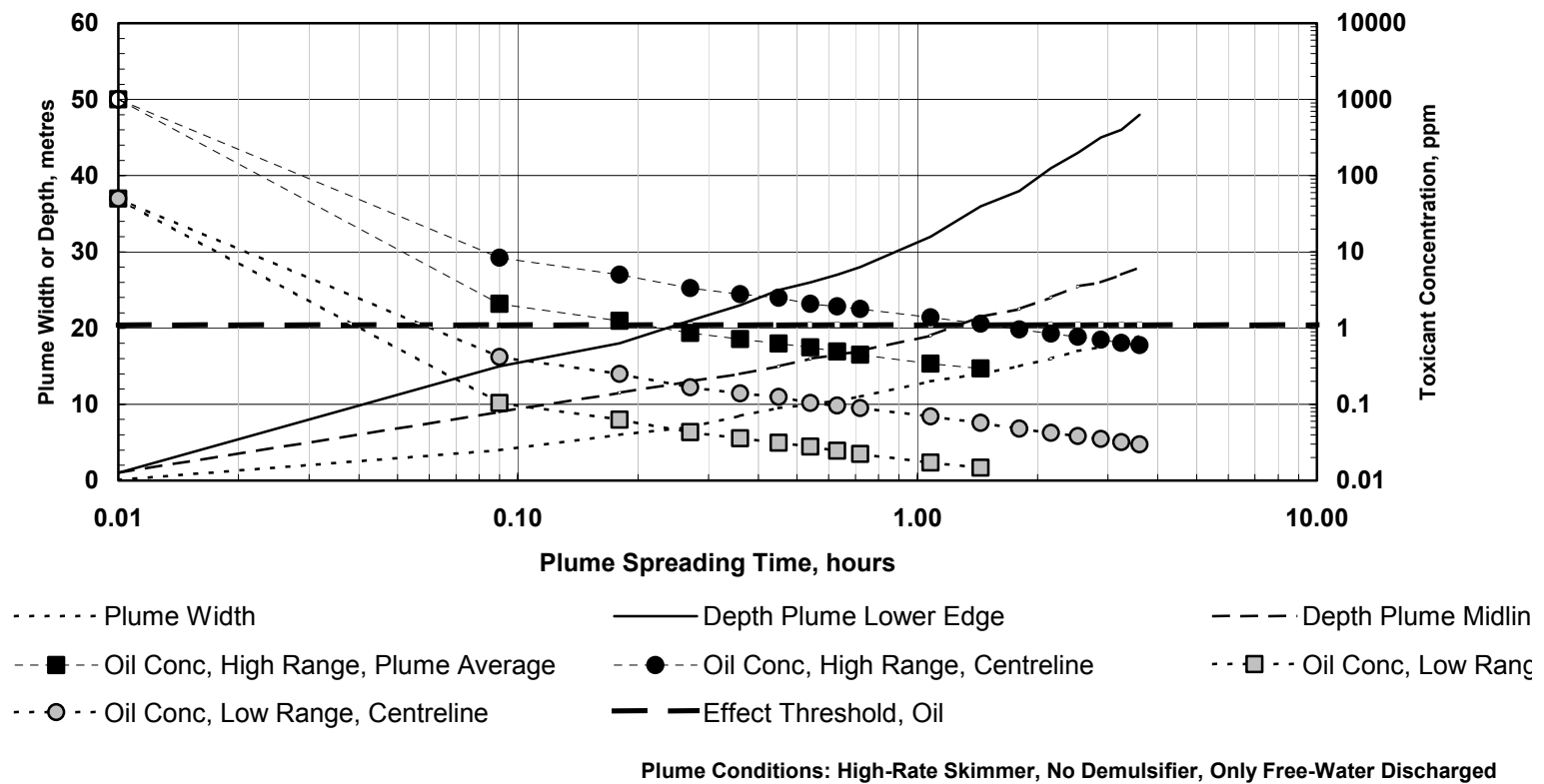


Figure 18. Plume Conditions: High-rated Skimmer Discharging Free Water Only

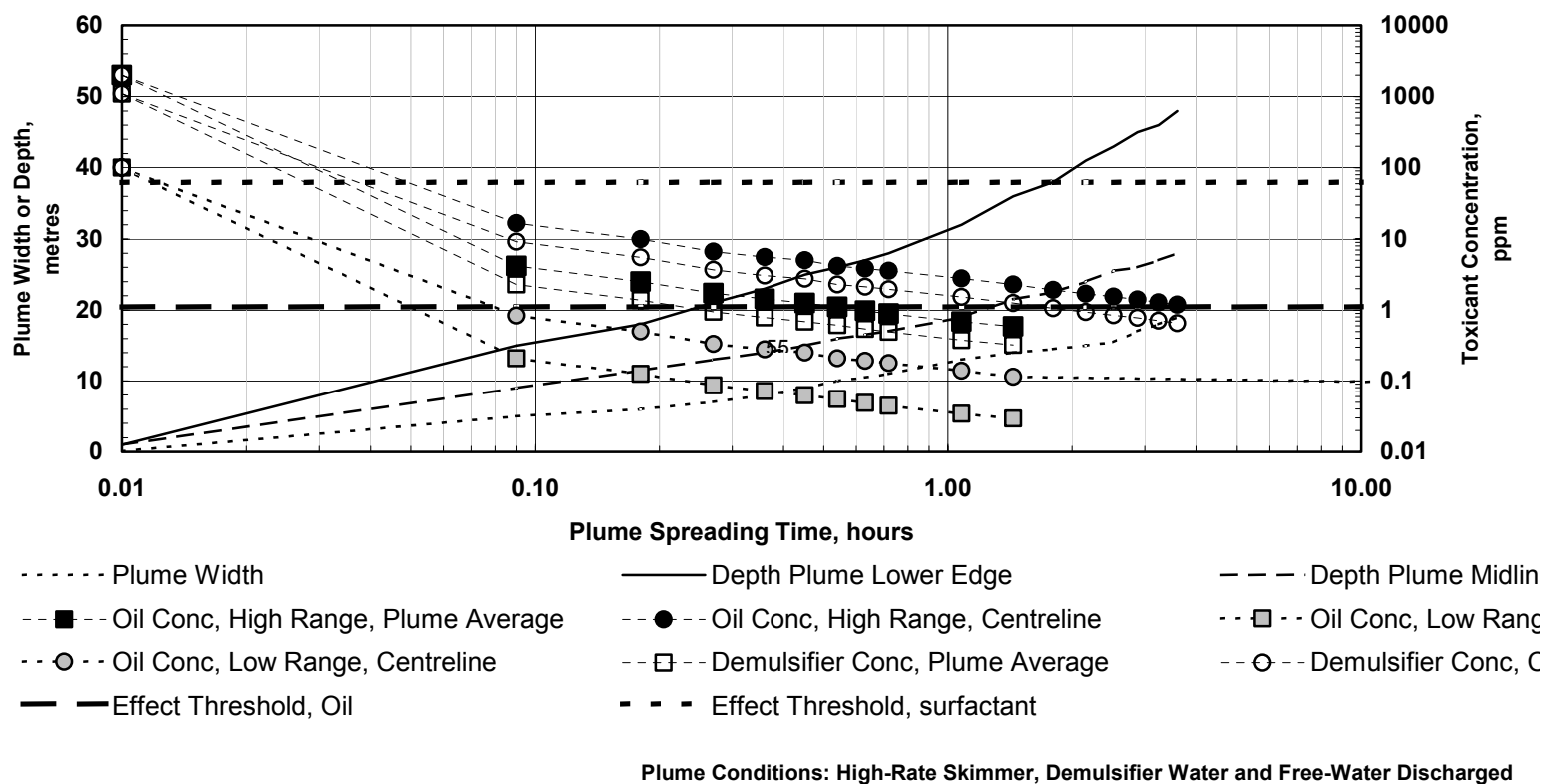
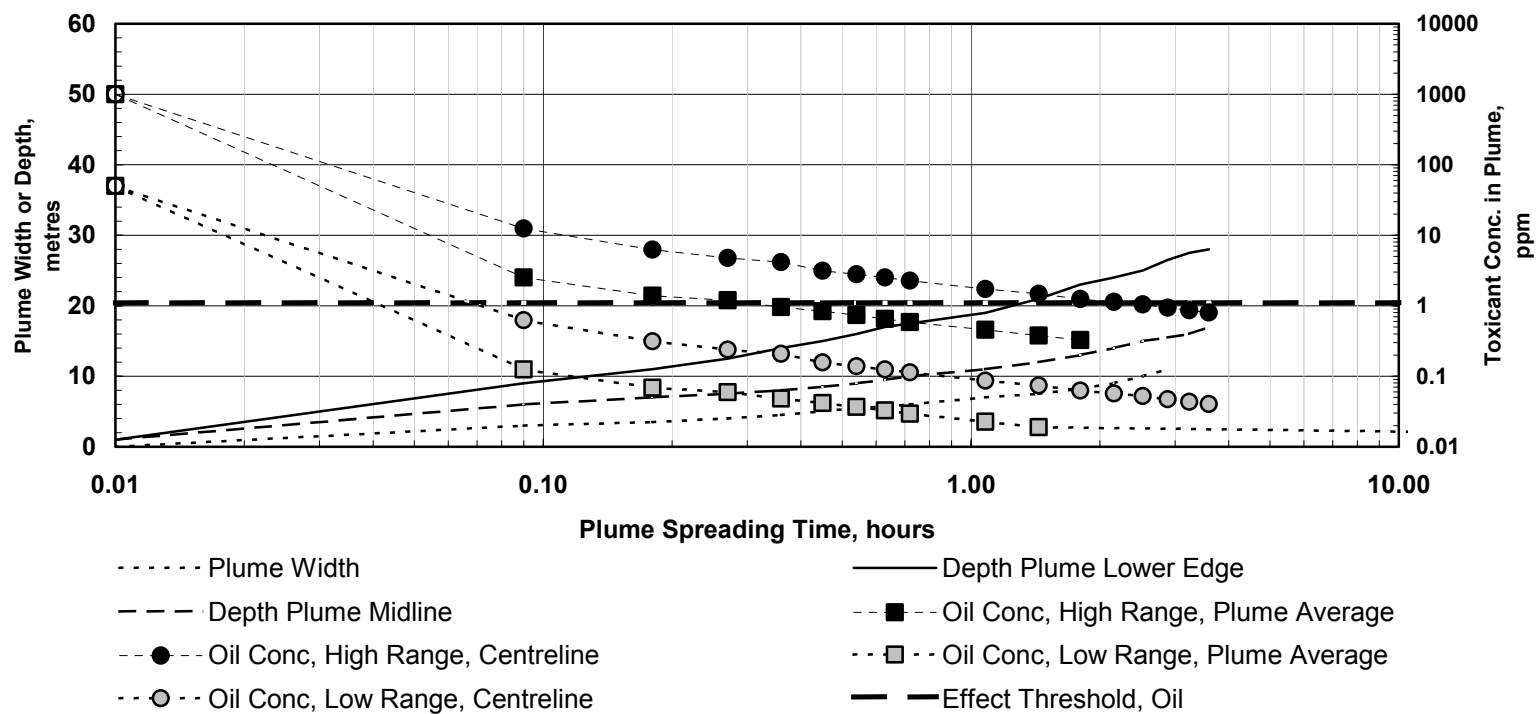
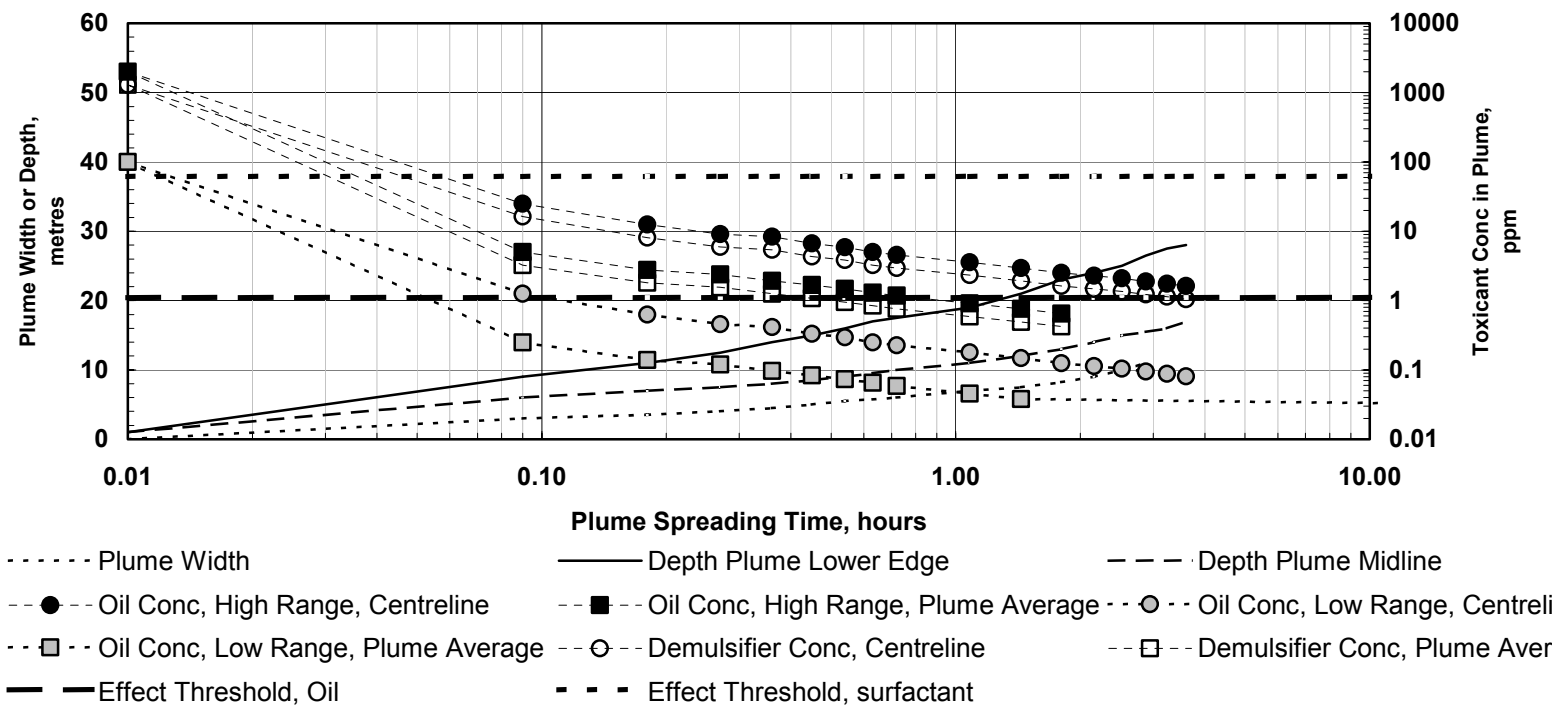


Figure 19. Plume Conditions: High-rated Skimmer Discharging Emulsion Water and Free Water



Plume Conditions: OSRO Standard, No Demulsifier, Only Free-Water Discharged

Figure 20. Plume Conditions: OSRO Guidelines, Discharging Free Water Only



Plume Conditions: OSRO Standard, With Demulsifier, Demulsified and Free Free-Water Discharged

Figure 21. Plume Conditions: OSRO Guidelines Skimmer Discharging Emulsion Water and Free Water

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